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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF MOLECULAR ORIENTATION AND NUCLEAR EXCHANGE IN SINGLE CRYSTALS OF MORPHOLINE N-OXIDE

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THESIS

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF MOLECULAR ORIENTATION AND NUCLEAR EXCHANGE IN SINGLE CRYSTALS OF MORPHOLINE N-OXIDE

by

Gary Lee Weerts

Thesis Advisor: W.M. Tolles

DEC 1971

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Electron Paramagnetic Resonance Studies of Molecular Orientation and Nuclear Exchange in Single Crystals of Morpholine N-oxide

by

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Lieutenant, United States Navy
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ABSTRACT

Low temperature (-150°C) EPR spectra of the nitroxide generated photolytically in a single crystal of N-nitromorpholine are complicated by the presence of two magnetically distinct orientations of the N-0 bond within the crystal. As the temperature is raised, the spectra are further complicated by motional effects. Since at -150° the molecule is essentially frozen in the crystal lattice with respect to the time of the EPR interaction, and since the nitrogen coupling tensor is markedly anisotropic, the observed EPR spectrum varies widely as the orientation of the applied field changes. The anisotropy of the nitrogen coupling tensor made it possible to unequivocally determine the orientation of the crystal with respect to the applied magnetic field. A series of experimental spectra was then obtained for several combinations of crystal orientation and temperature. In addition, computer programs were developed which simulate low, intermediate, and high temperature EPR spectra. By using a combination of experimental spectra and these programs, it was possible to determine the angle between the two orientations of the N-0 bond in the crystal and also to determine the energy barrier to exchange.

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I. INTRODUCTION

A. BACKGROUND

EPR studies of paramagnetic species trapped in solids may be conveniently classified according to the matrix in which the species is caged. Some common classifications are powders, glasses (frozen solutions), host crystals and single crystals. Each class has its own advantages and disadvantages, depending on the particular experimental situation. In general, however, if the experimental situation lends itself to the use of single crystals, then it will be found that single crystal EPR studies are to be preferred over the other types. In particular, since the species to be studied is regularly oriented within the crystal matrix, it is possible to determine the directional dependence and magnitude of anisotropic effects such as the dipole-dipole interaction. A set of orthogonal crystal axes can be assigned on the basis of the outward appearance of the crystal, and then these crystal axes may be used to determine the orientation of the crystal within an applied magnetic field. In addition, direction cosine matrices can be experimentally determined which relate the principal axes of the coupling tensors to the crystal axes and thus to the direction of the applied field.

B. PREVIOUS RESEARCH

Single crystal EPR studies of the nitroxide of N-nitromorpholine (hereafter referred to as morpholine N-oxide) by Bodnar [1] showed the

presence of two magnetically distinct sites at room temperature. The sites were characterized as a single nitrogen nucleus and two equivalent pairs of protons. Interchange between the axial and equatorial protons at room temperature was sufficiently rapid to cause an averaging effect so that hyperfine coupling for each pair of β protons could be labeled as $A_H = \frac{1}{2}(A_{ax} + A_{eq})$.

Bodnar developed the following set of hyperfine coupling tensors for morpholine N-oxide (expressed as column vectors):

Table I: Hyperfine Coupling Tensors for Morpholine N-oxide

Nucleus		Principal Values and Direction Cosines		
		$A_{xx} = 8.6$ G	$A_{yy} = 9.4$ G	$A_{zz} = 31.3$ G
N^{14}	x	0.83	-0.17	0.54
	y	0.23	0.97	-0.03
	z	-0.52	0.15	0.84
		$A_{xx} = 13.6$ G	$A_{yy} = 11.3$ G	$A_{zz} = 11.4$ G
4H	x	0.84	0.42	0.34
	y	0.01	0.62	-0.78
	z	-0.54	0.66	0.52

Windle, Kuhnle, and Beck [2] studied the EPR spectra of morpholine N-oxide in methylene chloride over a temperature range of -130° to + 120°C and found that the sum of the axial and equatorial hydrogen coupling constants increased with decreasing temperature.

C. OBJECT OF THIS RESEARCH

The primary goal of this research was the development of tools which would simulate the behavior exhibited by complex paramagnetic systems of the sort typified by morpholine N-oxide. These tools could then be applied to the secondary research aims of:

1. Refinement of the observed coupling constants of the morpholine N-oxide radical, including variations with temperature and crystal orientation.

2. Simulation of EPR spectra in the absence (or presence) of motional effects.

3. Determination of the angle between the magnetically distinct orientations of the N-0 bond in morpholine N-oxide at low temperatures.

4. Determination of the energy barrier to nuclear exchange for morpholine N-oxide in a matrix of N-nitromorpholine

5. Identification of the directions and magnitudes of the dipole-dipole and Fermi Contact interactions which occur in complex paramagnetic systems of this sort.

II. THEORY AND DEVELOPMENT OF THE MODEL

A. THE APPROPRIATE HAMILTONIAN

Carrington and McLachlan [3] characterize the spin Hamiltonian for the EPR interaction of one unpaired electron near a single nucleus as:

$$\mathcal{H} = \beta \vec{H} \cdot \overset{\rightrightarrows}{g} \cdot \vec{S} + \vec{S} \cdot \overset{\rightrightarrows}{A} \cdot \vec{I} - g_n \beta_n \vec{H} \cdot \vec{I}$$

The terms in the Hamiltonian respectively describe the contributions to the total energy which are due to interactions between the applied field and the unpaired electron, the electron and the nucleus, and the applied field and the nucleus. The first term represents the interaction between the applied field $\vec{H}$ and the spin moment $\vec{S}$ of the unpaired electron (electronic Zeeman energy). β is the Bohr magneton, and $\overset{\rightrightarrows}{g}$ is the spectroscopic splitting tensor. The second term is a combination of two terms and represents the hyperfine interaction between $\vec{S}$ and the nuclear spin $\vec{I}$. (Fermi Contact and dipole-dipole interactions.) $\overset{\rightrightarrows}{A}$ is the hyperfine interaction tensor. The third term represents the interaction between the applied field and the nuclear spin (nuclear Zeeman energy). g_n is the spectroscopic splitting factor for the nucleus, and β_n is the nuclear magneton.

1. The g-Tensor and the Electronic Zeeman Energy

In the absence of spin-orbit coupling, the g-tensor is isotropic and $\vec{S}$ represents the true spin of the electron. However,

when the electron possesses both spin and orbital angular momentum, the g-tensor is anisotropic, and $\vec{S}$ no longer represents the true electron spin since the spin is not oriented precisely along the field direction. An acceptable way to treat this problem is [4] to assume the existence of an "effective" field, such that the effective field direction is along the direction of quantization of the electron spin vector. The development is as follows:

The principal values of the g-tensor can be determined by choosing as system axes the principal axes of the tensor. If g_{xx}, g_{yy}, g_{zz} are the principal values of the g-tensor, and γ_x, γ_y, γ_z are the direction cosines of the applied magnetic field in the principal axis system, then $\vec{H} \cdot \vec{\vec{g}} = H(g_{xx} \gamma_x \hat{i} + g_{yy} \gamma_y \hat{j} + g_{zz} \gamma_z \hat{k})$. The vector quantity in parentheses can be more simply expressed as $g_{eff}\vec{h}$, where [4] $g_{eff} = [(g_{xx} \gamma_x)^2 + (g_{yy} \gamma_y)^2 + (g_{zz} \gamma_z)^2]^{\frac{1}{2}}$ and $\vec{h}$ is the unit vector along which the electron spin is quantized. Then $\vec{H} \cdot \vec{\vec{g}} = H g_{eff} \vec{h} = g_{eff} \vec{H}_{eff}$. Finally, the electronic Zeeman interaction becomes $\mathcal{H} = g_{eff} \vec{H}_{eff} \cdot \vec{S}$.

2. The A-Tensor, the Fermi Contact Interaction and the Dipole-Dipole Interaction

The second term of the spin Hamiltonian may be separated into an isotropic part $a\vec{S} \cdot \vec{I}$ and an anisotropic part $\vec{S} \cdot \vec{\vec{T}} \cdot \vec{I}$. Thus the A-tensor can be represented as: $\vec{\vec{A}} = \vec{\vec{T}} + a\vec{1}$.

The isotropic part $a\vec{S} \cdot \vec{I}$ arises from the Fermi Contact interaction which represents the hyperfine coupling between the nuclear

spin moment and the magnetic field produced at the nucleus by the spinning electron. The contact interaction can only occur when the electron has a finite probability density at the nucleus [3].

The anisotropic part $\vec{S}\cdot\vec{\vec{T}}\cdot\vec{I}$ is due to magnetic coupling between the magnetic moments of the electron and nucleus. This dipolar portion of the Hamiltonian is given by

$$\vec{S}\cdot\vec{\vec{T}}\cdot\vec{I} = g_n \beta_n g \beta \left[\frac{\vec{S}\cdot\vec{I}}{r^3} - \frac{3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5}\right]$$

where $\vec{r}$ is the radius vector between the two moments, and r is the distance between them. The dipolar portion of the Hamiltonian averages out to zero whenever the electron cloud is spherical [3].

3. Combined Effects of the Fermi Contact, Dipole-Dipole and Nuclear Zeeman Interactions

The second and third terms of the spin Hamiltonian may be combined as

$$\vec{S}\cdot\vec{\vec{A}}\cdot\vec{I} - g_n \beta_n \vec{H}\cdot\vec{I} = (\vec{S}\cdot\vec{\vec{A}} - g_n \beta_n \vec{H})\cdot\vec{I}.$$

In addition, $\vec{S}$ may be represented as $m_s\vec{h}$, where m_s is the spin quantum number of the electron ($\pm\frac{1}{2}$) and $\vec{h}$ is a unit vector in the direction of the applied field. Substituting above and rearranging gives

$$\vec{S}\cdot\vec{\vec{A}}\cdot\vec{I} - g_n \beta_n \vec{H}\cdot\vec{I} = -g_n \beta_n \left(\vec{H} - \frac{m_s\vec{h}}{g_n \beta_n}\cdot\vec{\vec{A}}\right)\cdot\vec{I} = -g_n \beta_n \vec{H}'_{eff}\cdot\vec{I}$$

4. Resultant Hamiltonian for the General Case

Using the expressions developed in sections 1 and 3 above, and expanding to the case of a single electron interacting with several

nuclei, the spin Hamiltonian becomes

$$\mathcal{H} = \beta g_{eff} \vec{H}_{eff} \cdot \vec{S} - \sum_{i} (g_n \beta_n \vec{H}'_{eff} \cdot \vec{I}_i)$$

where I_i is the spin of the i-th nucleus.

B. PROGRAM ESRPLT

The Hamiltonian given in section A-4 above was used as the basis for a computer program which would predict and plot complex EPR spectra in the absence of motional effects. The mechanics of this program, called ESRPLT, are given in Appendix I.

C. PROGRAM NITROX

A second computer program was developed which was based on a simpler treatment of the EPR interaction than the approach used in ESRPLT. This program, called NITROX, makes use of the high field approximation [5, 6], which assumes that the nuclear Zeeman effects (NMR transitions) are insignificant compared to the electronic Zeeman effects (EPR transitions).

NITROX was designed to compute coupling constants for a nitroxide as a function of the direction of the applied field. Coupling constants were formulated using a variation on the method employed by Lefebvre and Maruani [6]

$$A = [(A_{xx} \gamma_x)^2 + (A_{yy} \gamma_y)^2 + (A_{zz} \gamma_z)^2]^{\frac{1}{2}}$$

where A is the computed coupling constant, A_{xx}, A_{yy}, A_{zz} are the

principal values of the input coupling tensor, and γ_x, γ_y, and γ_z are the direction cosines of the applied field in the principal axis system. (Note the similarity of this approach to the method used to compute g_{eff}.)

NITROX also computes the energies and intensities of the lines of the first order EPR spectrum, plots the spectrum, and punches cards which contain energy-intensity data in a format which is required by program GEX. This program is adequate for the simulation of EPR spectra in the presence or absence of motional effects. The mechanics of program NITROX are given in Appendix II.

D. PROGRAM GEX

A third computer program, developed by Tolles [7], simulates the shape of an EPR spectrum as a function of the rate of exchange.

III. EXPERIMENTAL

A. IDENTIFICATION OF CRYSTAL AND PRINCIPAL AXES

1. Assignment of Crystal Axes

The crystal axes assigned for crystals of N-nitromorpholine were those used by Bodnar [1]. The orientation of these crystal axes relative to the physical appearance of the crystal is depicted in Figure 1.

2. Crystal Orientation in the EPR Spectrometer

The method used to suspend the crystal between the pole pieces of the EPR spectrometer is shown in Figures 2 and 3. A very thin layer of Kel F grease was used to make the crystal adhere to the flat ground surface of a quartz rod. The intent was to have the crystal aligned so that the + Z axis pointed toward the observer, and the + Y axis pointed downward when the quartz rod was viewed in a direction perpendicular to the flat ground face with the long extension of the rod pointed upward. Adjustments in the angle ϕ were accomplished by using a microscope equipped with a 360 - degree turntable and a cross-hair eyepiece. As the crystal was viewed along the + Z axis, clockwise rotation of the crystal about the Z axis corresponded to a counter-clockwise movement of the applied field, increasing ϕ. When the crystal was suspended between the pole pieces of the spectrometer, a pointer attached to an extension of the quartz rod indicated θ. Variation

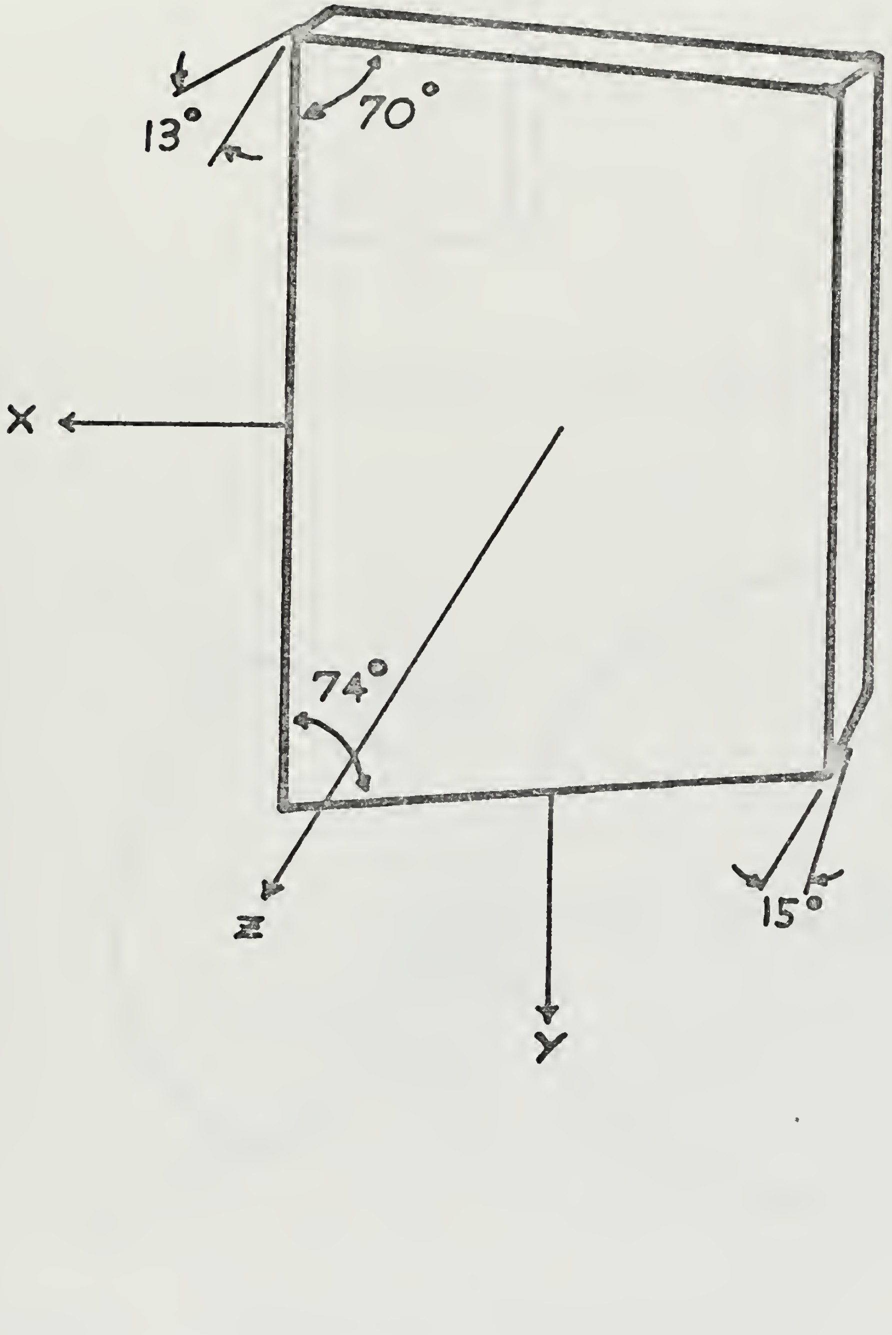

Figure 1. Crystal Form and Assigned Axes

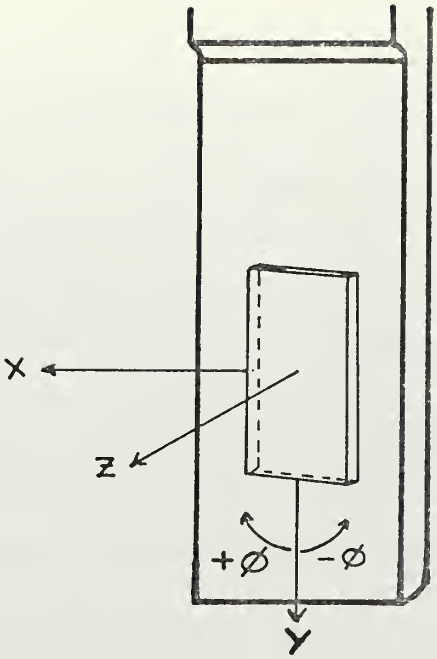

Figure 2. Crystal Orientation on the Quartz Rod

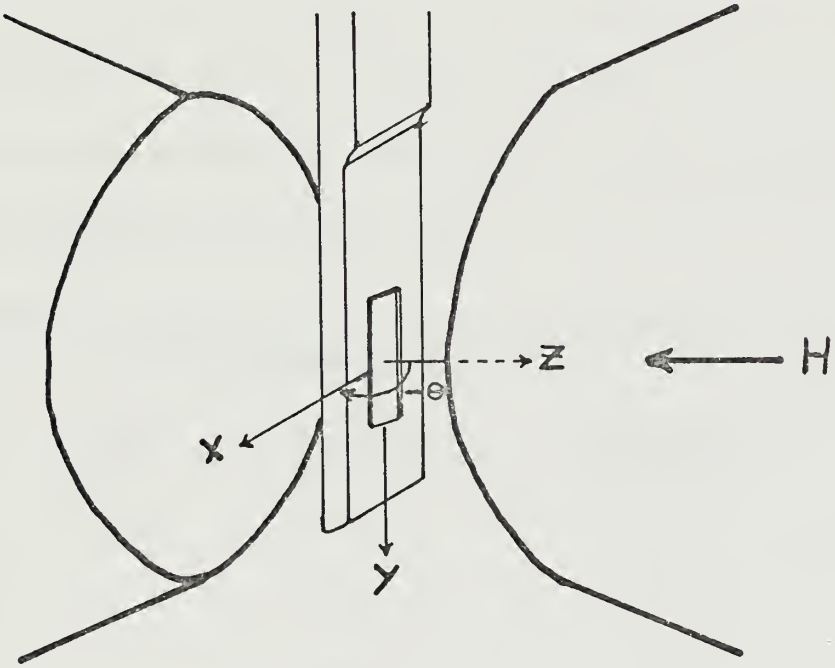

Figure 3. Alignment of the Crystal in the Magnetic Field of the EPR Spectrometer

of θ could be accomplished by moving this pointer. When viewed from the top, (along the -y axis), counter-clockwise rotation corresponded to a + change in θ.

It can readily be seen from Figure 1 that some ambiguity could easily arise in the determination of crystal orientation relative to an applied magnetic field. Once crystal axes have been assigned, it is theoretically possible to ascertain crystal orientation unequivocally. However, it is often difficult to discern from the physical appearance of the crystal whether or not one of the axes has been inverted. This ambiguity can be readily resolved, however, by making use of previously tabulated values of coupling constants [1] and by knowing the possible confusing orientations of the crystal. Some selected values for the coupling constants of morpholine N-oxide at room temperature are tabulated in Table II versus the orientation of the applied field (polar coordinates) relative to the crystal axes.

Table II: Room Temperature Coupling Constants for Morpholine N-oxide

θ(°)	∅(°)	A_N (Gauss)	A_H (Gauss)
0	-45	27.4	12.0
30	0	31.0	11.4
60	-45	24.2	11.7
120	0	8.8	13.7
120	-45	9.15	12.7

For any given orientation of the crystal, the possible axis transformations are

1. A 180-degree rotation about the X axis;
2. A 180-degree rotation about the Y axis;
3. A 180-degree rotation about the Z axis.

Since morpholine N-oxide is symmetric with respect to a reversal in the direction of the applied field, there is a pair of equivalent polar coordinate angles corresponding to a 180° rotation about any one of the crystal axes. These pairs of polar coordinate angles which arise from axis inversion can be seen to stem from changes in the signs of the elements of an identity matrix as the matrix is subjected to the operations stated above. Consider the identity matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

where the first, second, and third row non-zero elements correspond respectively to

$$x = \sin\theta \cos\phi$$

$$y = \sin\theta \sin\phi$$

$$z = \cos\theta$$

It can now be seen that the following relationships hold

1. For a 180° rotation about the x axis we have

$$\begin{bmatrix} 1 & & \\ & -1 & \\ & & -1 \end{bmatrix}^{\underline{H}} \quad \begin{matrix} \theta \longrightarrow 180^\circ - \theta \\ \phi \longrightarrow -\phi \end{matrix} \qquad \text{or} \qquad \begin{bmatrix} -1 & & \\ & 1 & \\ & & 1 \end{bmatrix}^{-\underline{H}} \quad \begin{matrix} \theta \longrightarrow \theta \\ \phi \longrightarrow 180^\circ - \phi \end{matrix}$$

2. For a 180° rotation about the y axis we have

$$\begin{bmatrix}-1 & & \\ & 1 & \\ & & -1\end{bmatrix}^{\underline{H}} \begin{matrix}\theta \rightarrow 180° - \theta \\ \phi \rightarrow 180° - \phi\end{matrix} \quad \text{or} \quad \begin{bmatrix}1 & & \\ & -1 & \\ & & 1\end{bmatrix}^{-\underline{H}} \begin{matrix}\theta \rightarrow \theta \\ \phi \rightarrow -\phi\end{matrix}$$

3. For a 180° rotation about the z axis we have

$$\begin{bmatrix}-1 & & \\ & -1 & \\ & & 1\end{bmatrix}^{\underline{H}} \begin{matrix}\theta \rightarrow \theta \\ \phi \rightarrow 180° + \phi\end{matrix} \quad \text{or} \quad \begin{bmatrix}1 & & \\ & 1 & \\ & & -1\end{bmatrix}^{-\underline{H}} \begin{matrix}\theta \rightarrow 180° - \theta \\ \phi \rightarrow \phi\end{matrix}$$

In general, the particular set of θ, ϕ selected to represent a rotation about a given crystal axis was chosen such that it was physically possible to accomplish the orientation change using the standing set-up of the EPR spectrometer.

3. Principal Axis Systems

The directions, in the crystal axis systems, of the principal axes of the several coupling tensors can be extracted from the appropriate matrix of direction cosines. The directions of the principal axes of the nitrogen coupling tensor were determined using the matrix of direction cosines found on page 11. The orientations of these principal axes relative to the crystal axes are shown in Figure 4.

4. The Angle Alpha

The angle alpha was defined as one-half of the angular displacement which exists between the orientations of the N-0 bond. This assignment was a matter of convenience since the basic direction cosine matrix for the nitrogen coupling tensor was the result of room temperature observations. At room temperature the exchange rate is

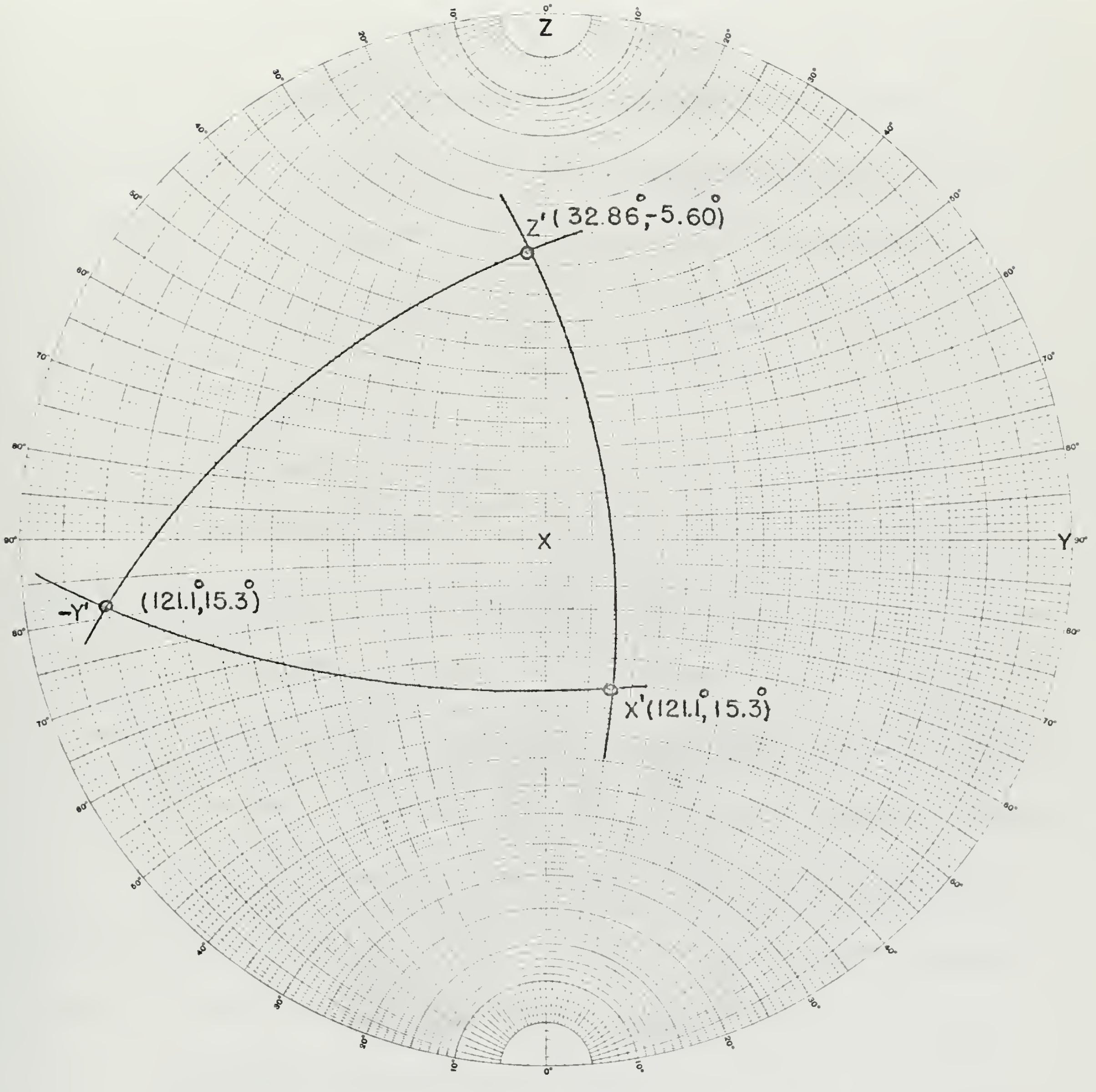

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Figure 4. Stereographic Projection Showing Relative Orientations of Crystal (X, Y, Z) and N^{14} Principal Axes (X', Y', Z')

high enough so that what is seen is the averaged orientation of the principal axes (i.e., alpha = 0 on the average). When the exchange rate is slow relative to the time of the EPR interaction, each orientation of the N-0 bond results in a separate contribution to the observed spectrum. Thus alpha was taken as the angle between the "average" orientation at room temperature and either of the two contributing orientations at low temperatures.

B. EXPERIMENTAL SPECTRA

1. The EPR Spectrometer

The EPR spectrometer used was a Varian model V-4502-13 (X-band), with Fieldial V-F-2503 magnetic field regulation for the nine-inch magnet. The modulation frequency used was 100 KC. The EPR cavity was contained within a Dewar flask to facilitate low temperature studies. Temperature regulation was accomplished by directing a stream of cold nitrogen gas through a thermostatted heating unit at the base of the Dewar flask and into the cavity. Cavity temperature was measured by means of a copper-Constantan thermocouple.

2. Synthesis of Morpholine N-oxide

The morpholine N-oxide radical was generated by irradiating single crystals of N-nitromorpholine with ultraviolet light. The source used was a Christie Xenolite Model UF10JKK xenon-mercury vapor lamp.

3. Spectra Recorded

Spectra were recorded for six crystal orientations at temperatures ranging from + 30° to -150°C. The orientations chosen were defined by the room temperature principal axis system of the nitrogen coupling tensor. The magnetic field was oriented successively along the Z, Y and X principal axes and the XZ, XY, and YZ diagonals. The relationships of these principal axes to molecular structure was proposed by Bodnar [1]. The Z axis is directed along the nitrogen $2P_{\pi}$ orbital where the unpaired electron is expected to be most highly localized. The Y axis is directed along the N-0 bond, and the X axis is perpendicular to the plane containing the N-0 bond and the nitrogen $2P_{\pi}$ orbital. These orientations were chosen because it was expected that they would be most useful in the determination of the angle alpha. The temperature range was dictated by a combination of crystal melting point (51° - 52°C), the temperature regulation system, and the observable changes in the EPR spectra as temperature was lowered. Table III gives a summary of spectra recorded.

Table III: Summary of Experimental Spectra

Magnetic Field Orientation		Temperature
Crystal Axes (θ,ϕ)	N^{14} Principal Axes	°C
(32.86, -5.60)	Z axis	20,0,-15,-25,-50,-150
(81.37, 99.90)	Y axis	20,0,-50,-100,-150
(121.5, 15.3)	X axis	0,20,-15,-25,-105,-150
(77.5, 8.5)	XZ diagonal	29,20,0,-15,-50,150
(117.5, -37.0)	XY diagonal	20,0,10,-15,-50,-150
(60.5, -54.5)	YZ diagonal	31,30,15,0,-15,-30 -50,-150

C. SIMULATED SPECTRA

1. The g-Tensor

The principal axes of the g-tensor were assumed to coincide with the principal axes of the nitrogen coupling tensor. The principal values of g used were determined by Griffith, Cornell, and McConnell [8]. The values of g_{xx}, g_{yy}, and g_{zz} used were 2.0061, 2.0089, and 2.0027 respectively. (Note the interchange in assignments of the X and Y axes.)

2. Determination of the Angle Alpha

The spectra which were simulated for the determination of alpha were those which were estimated to be the most likely to show a large variation in the simulated spectrum for a small change in alpha. In addition, it was assumed that any changes in molecular orientation could be represented as angular rotations about a vector perpendicular

to the plane containing the $N^{14} - 2P_{\pi}$ orbital and the N-0 bond. Consequently, the magnetic field orientations chosen were (principal axis system):

a. Along the Z axis (nitrogen $2P_{\pi}$ orbital),

b. Along the Y axis (N-0 bond),

c. Along the YZ diagonal (midway between the N-0 bond and the $2P_{\pi}$ orbital in the YZ plane).

3. Determination of the Rate of Exchange

An inspection of experimental spectra revealed that the series of spectra which showed the most clearly distinguishable changes with changing temperature were those for the case where the applied field was directed midway between the X principal axis and the $2P_{\pi}$ orbital in the XZ plane ($\theta = 77.5°$, $\emptyset = 8.5°$ crystal axis system). As a result this orientation was chosen for exchange studies. Program NITROX was used to compute the line energies and intensities which make up the spectrum for the case of no exchange, and the punched output was used, in turn, as input data for program GEX. GEX was then used to simulate the spectrum changes as a function of the rate of exchange.

IV. RESULTS AND OBSERVATIONS

A. COUPLING CONSTANT VARIATION - EXPERIMENTAL SPECTRA

The hyperfine coupling constants which were observed for morpholine N-oxide at -150°C are summarized in Table IV.

Table IV: Hyperfine Coupling Constants for
Morpholine N-oxide at -150°

Nucleus	Values Observed (Gauss)		
	A_{XX}	A_{YY}	A_{ZZ}
N^{14}	7.17	7.8	33.8
axial H^1	23.0	21.8	23.3
equatorial H^1	7.3	2.2	2.3

Note 1: Hydrogen coupling constants are those observed along the N^{14} principal axes and are not true principal values.

1. Observed N^{14} Coupling Constants

The N^{14} coupling constants observed for magnetic field orientations along the principal axes of the nitrogen coupling tensor are recorded as a function of temperature in Table V and are depicted in Figure 5.

Two interesting observations may be made regarding this data. First, the average of the principal values of the coupling constants at -150°C is 16.26 gauss, which is in good agreement with the isotropic value of 16.8 gauss (-100°C) reported by Windle, Kuhnle and Beck [2].

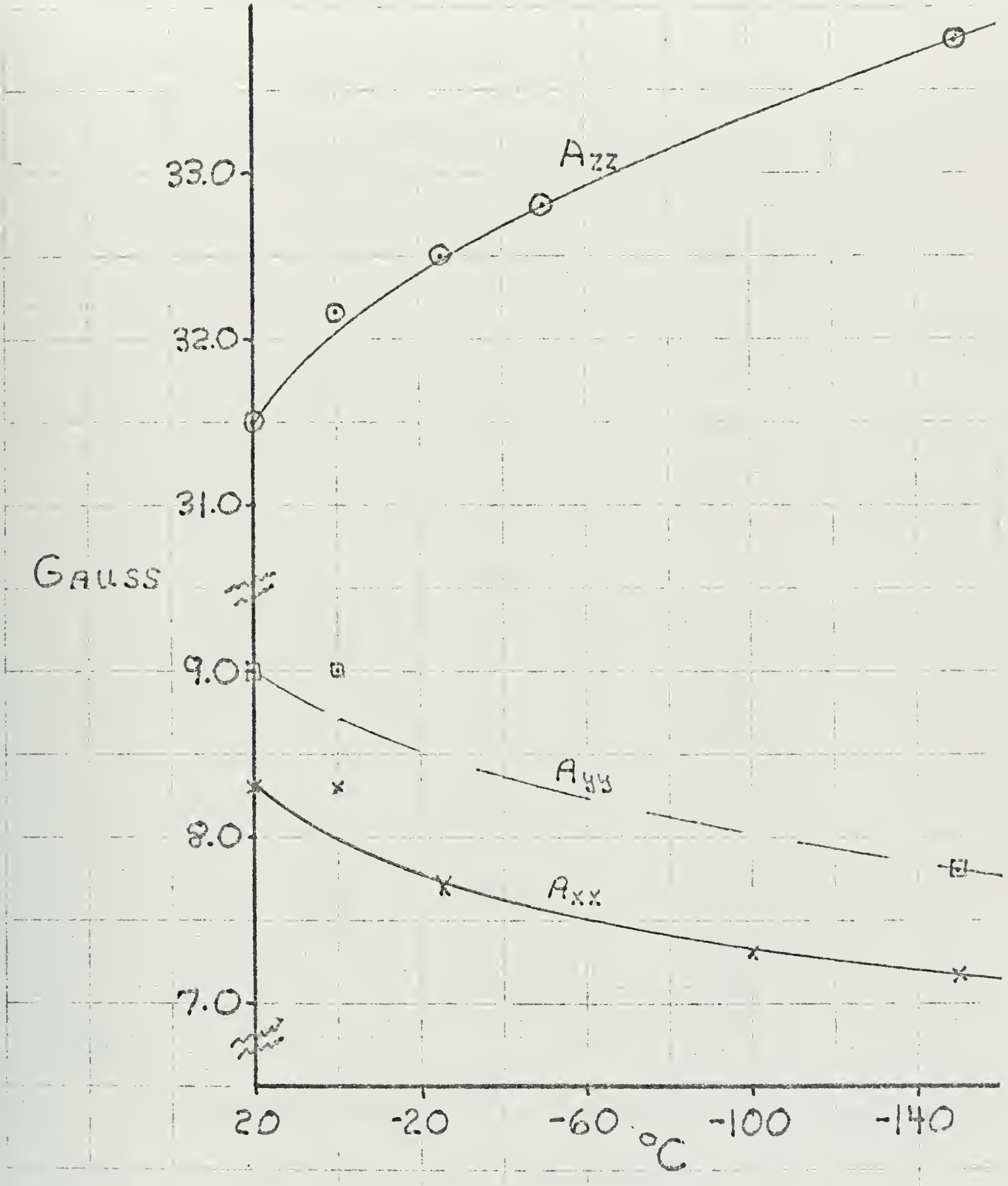

Figure 5. N^{14} Hyperfine Coupling Constants versus Temperature

Second, and perhaps even more interesting, is the observation that the average of the coupling constants at 20°C and -150°C are, for practical purposes, the same (16.27 vs 16.26 gauss).

Table V: N^{14} Coupling Constants as a Function of Temperature

	C.C (gauss)	T(°C)
A_{XX}	8.3	20
	8.3	0
	7.7	-25
	7.3	-100
	7.17	-150
A_{YY}	9.0	20
	9.0	0
	-[1]	-50
	-	-100
	7.8[2]	-150
A_{ZZ}	31.5	20
	32.17	0
	32.5	-25
	32.8	-50
	33.8	-150

Notes:

1. Some coupling constants were impossible to determine from experimental spectra because of poor resolution.

2. This coupling constant was determined using a combination of experimental and simulated spectra.

2. Observed Hydrogen Coupling Constants

Particular observations, such as those made for the N^{14} coupling constants, cannot presently be made regarding the coupling constants for the β protons. A few general observations, however, are possible from the data which was recorded.

a. Anisotropy in the coupling constant was definitely observable as the temperature was lowered. Although the separate principal axis systems for the axial and equatorial protons were not determined at low temperatures, spectra recorded for magnetic field orientations along the N^{14} principal axes indicate the presence of distinct coupling tensors for the two kinds of β protons.

b. The values of the axial proton coupling constants observed along the N^{14} principal axes did not vary widely (21.8 to 23.3 gauss) relative to the equatorial coupling constants for the same orientations (7.3 to 2.2 gauss). The lower figure for the equatorial proton coupling constant was estimated based on experimental and simulated spectra.

B. SPECTRUM VARIATION WITH TEMPERATURE

As the temperature was lowered from 20° to -150°C, the recorded spectra showed several distinct changes which were independent of the direction of the applied field.

1. Resolution became poorer as the temperature was lowered. Lines broadened and disappeared, or coalesced into new or already existing lines.

2. Coupling constants associated with N^{14} increased or decreased, depending on the orientation of the applied field. This effect was noted previously and will not be discussed further here.

The decrease in spectrum resolution which occurred as temperature was lowered below 20°C is directly related to the rate of interconversion between alternative conformations of the radical species. The effect on the spectrum of the rate of exchange of the axial and equatorial protons is shown by the correlation diagram in Figure 6. The base spectrum for a low rate of exchange is that which would result from the coupling of a single N^{14} nucleus with two inequivalent pairs of protons (as is the case for morpholine N-oxide). However, because the existence of two separate orientations of the N-0 bond is distinguishable to the EPR spectrometer when exchange is slow, the correlation diagram represents only part of the reason for poor resolution. The simulated spectra in Figure 7 show another complicating factor. The spectrum at the top of the page is the one which would exist if only a single orientation of the N-0 bond were distinguishable. The superimposed spectra at the bottom of the page show what actually exists. At low exchange rates the observed spectrum is the composite of the superimposed spectra in Figure 7, and only nine distinguishable peaks represent a total of fifty-four contributing lines (see Figure 9). When

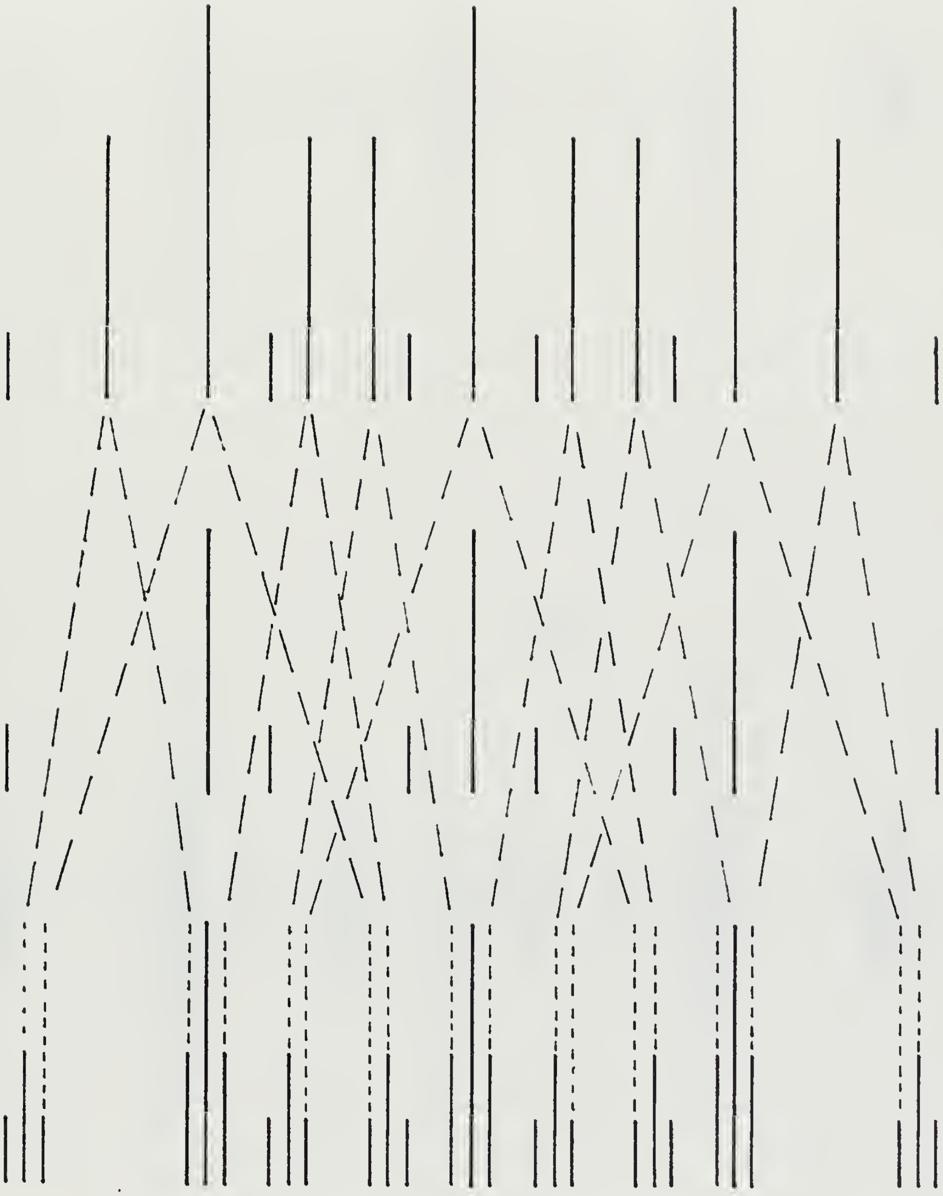

Figure 6. Correlation Diagram Showing the Effect on the Observed Spectrum of the Rate of Exchange of the Axial and Equatorial Protons. Bottom: slow exchange; Top: rapid exchange; Middle: intermediate case.

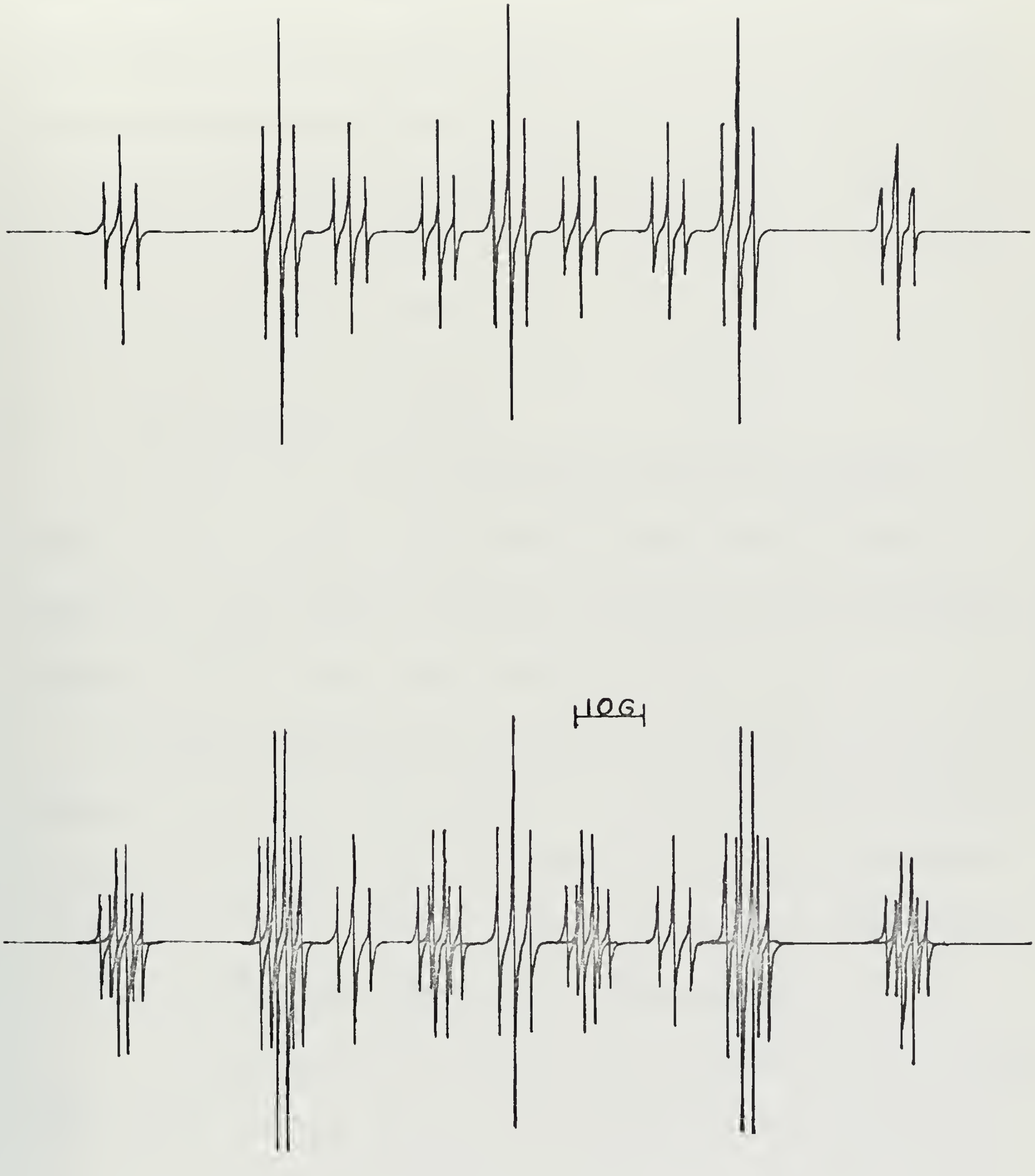

Figure 7. Top: Simulated Low Exchange Rate Spectrum for a Single Orientation of the N-O Bond
Bottom: Simulated Low Exchange Rate Spectrum for the Case Where Two Orientations of the N-O Bond Exist.

a high rate of exchange exists, molecular motion results in an averaged picture so that the top section of the correlation diagram is a good representation of the observable spectrum. An idea of the complexity of the observed spectrum at intermediate rates of exchange can be had by mentally superimposing slightly displaced correlation diagrams on the lower spectrum in Figure 7. (The 1:1:1 peaks would coalesce for the high rate of exchange case.)

C. DETERMINATION OF ALPHA

A combination of spectra recorded at -150°C and simulated spectra were used for the determination of alpha. As was noted previously, magnetic field orientations were chosen to lie in the plane containing the N^{14} $2P_{\pi}$ orbital and the N-0 bond.

After experimentation with both ESRPLT and NITROX, NITROX was chosen for further work since both programs produced identical spectra for the case of no exchange, and NITROX took about one-twentieth as much computer time. In addition, NITROX is the more flexible program.

1. N^{14} Coupling Constants - Simulated Spectra

The principal axis system used to represent the N^{14} coupling tensor was the one determined at room temperature. The existence of two orientations of the N-0 bond was simulated by displacements (by the angle alpha) away from these axes. Since the displacements were assumed to occur in the YZ principal axis plane, only the Y and Z input principal values could affect the predicted nitrogen coupling constant in

the simulated spectra. Taking the case where the applied field is along the Z principal axis, for instance, the computer determined the lines and intensities of the spectrum which would result from the application of a magnetic field (+) alpha degrees away from the Z axis in the YZ plane. It then computed the lines and intensities which would result from the application of the field (-) alpha degrees away from the Z axis in the YZ plane (field displaced toward (-)Y axis). Finally, it combined the two sets of lines and intensities into one composite spectrum.

Now the observed values of A_{ZZ} and A_{YY} for N^{14} were measured to be 33.8 and 7.8 gauss, respectively, at -150°C. These values include the effects caused by alpha. The trigonometric relationships which describe the variation in observed N^{14} Z and Y coupling constants with alpha and with the input principal values A_{ZZ} and A_{YY} are:

$$A_{ZZ}\text{ (observed)} = (A_{ZZ}^{2} \cos^{2}\alpha + A_{YY} \sin^{2}\alpha)^{\frac{1}{2}} = 33.8 \text{ gauss}$$

$$A_{YY}\text{(observed)} = (A_{YY}^{2} \cos^{2}\alpha + A_{ZZ} \sin^{2}\alpha)^{\frac{1}{2}} = 7.8 \text{ gauss.}$$

The variation of A_{ZZ} (input) and A_{YY} (input) with alpha which occurs for correct predicted output values is plotted in Figure 8.

Although there are any number of combinations of alpha, A_{ZZ} (input) and A_{YY} (input) which will result in a correct simulation of the observed spectrum for orientations of the magnetic field along the Y or Z principal axes, there is only one combination which will give the correct spectrum when the applied field is along the YZ diagonal (see section III, B.3. for clarification of this orientation).

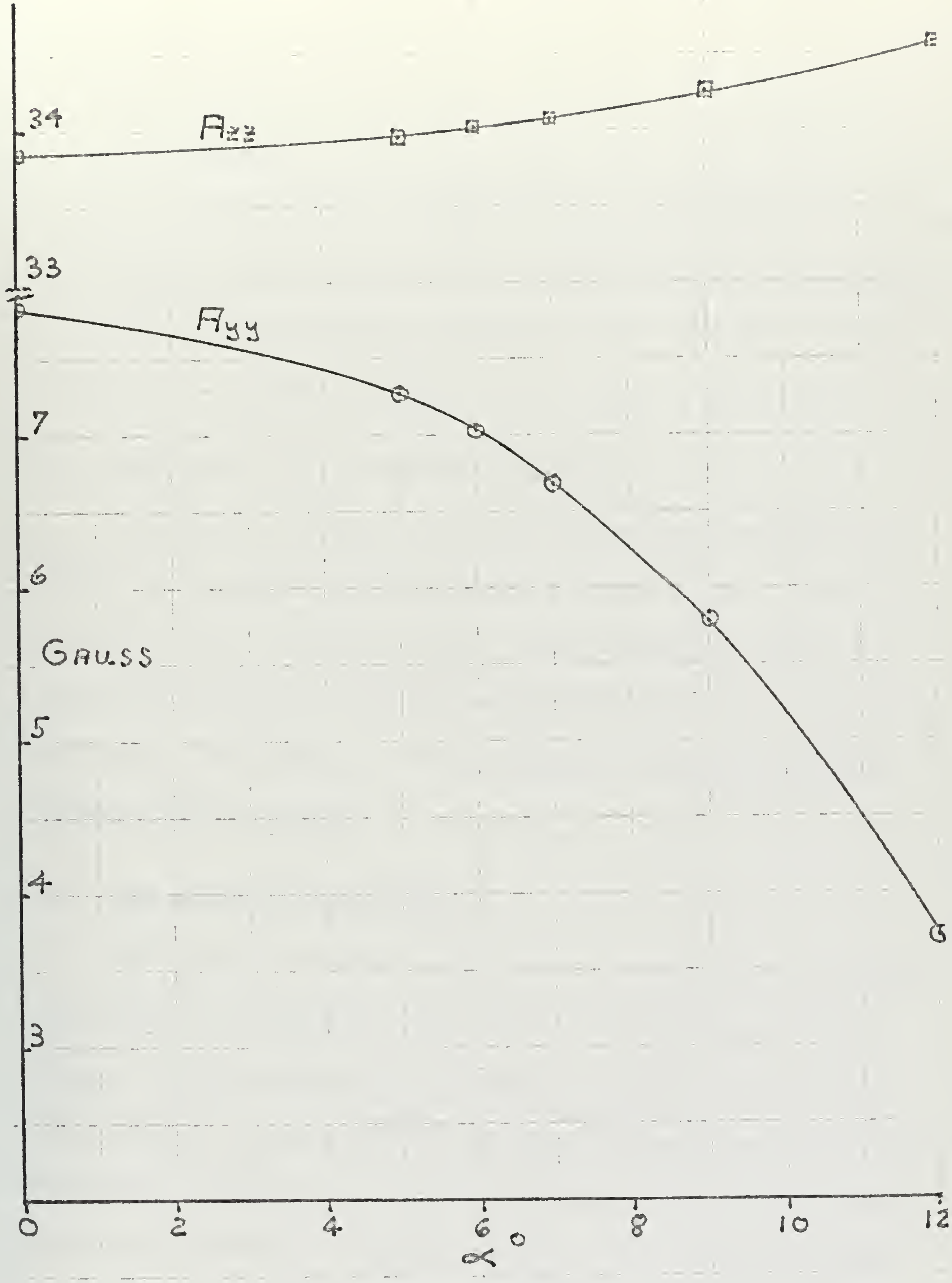

Figure 8. Variation of N^{14} Coupling Constants with Alpha. These Coupling Constants are Correct Input Values for Computer Simulation.

2. Alpha

By using input coupling constants from Figure 8 and assuming isotropic axial and equatorial proton coupling constants (as measured or estimated from experimental spectra), it was possible to determine a value of five degrees for alpha.

D. SIMULATED AND EXPERIMENTAL SPECTRA

Sets of experimental and simulated spectra for four different applied field orientations are compared in Figures 9, 10, 11, and 12. Regarding proton coupling constants, it can be seen that only in the case where the applied field was perpendicular to the $2P_{\pi}$ orbital/N-0 bond plane (Figure 12) was there a measurable (and large) equatorial proton coupling constant.

E. THE BARRIER TO EXCHANGE

The change in observed spectra which can result from a relatively small change in temperature can readily be seen from Figure 13. The magnetic field orientation used to obtain the spectra in Figure 13 was the one used in programs NITROX and GEX to determine the energy barrier to exchange. Because of the general similarity of all of the spectra for any given orientation for temperatures below -50°C, the most reliable data was obtained for temperatures greater than -50°C. The exchange rate data from program GEX were used to construct the Arrhenius rate plot depicted in Figure 14, where τ is the rate of interconversion between conformers. The data and the slopes of the two lines shown

in Figure 14 were used to calculate the free energy, the enthalpy, and the entropy of activation for the process of interconversion. The appropriate formulas are readily derived from the rate equation from absolute reaction rate theory:

$$k = \frac{k_B T}{h} \exp(-\Delta F^{\ddagger}/RT) = \frac{k_B T}{h} \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT)$$

The data and the results of the calculations are given in Table VI.

Table VI: Data and Results Relative to Rate of Conformer Interconversion

T(°C)	τ(sec)	$1/T$(°K)	$\log_{10}(\frac{1}{\tau})$
29	2.14×10^{-9}	3.31×10^{-3}	8.67 (+0.30,-0.18)
20	4.28×10^{-9}	3.41×10^{-3}	8.37 (+0.19,-0.10)
0	1.50×10^{-8}	3.66×10^{-3}	7.82 (+0.07,-0.06)
-15	1.93×10^{-8}	3.88×10^{-3}	7.72 (+0.14,-0.11)

$\Delta F^{\ddagger} = 5.86 \pm 0.16$ kcal/mole

$\Delta H^{\ddagger} = 7.21 \pm 1.26$ kcal/mole

$\Delta S^{\ddagger} = 4.43 \pm 4.71$ cal/mole °K

The value calculated for $\Delta F^{\ddagger}$ agrees very closely with the value of 5.7 ± 0.2 kcal/mole by Windle, Kuhnle and Beck [2].

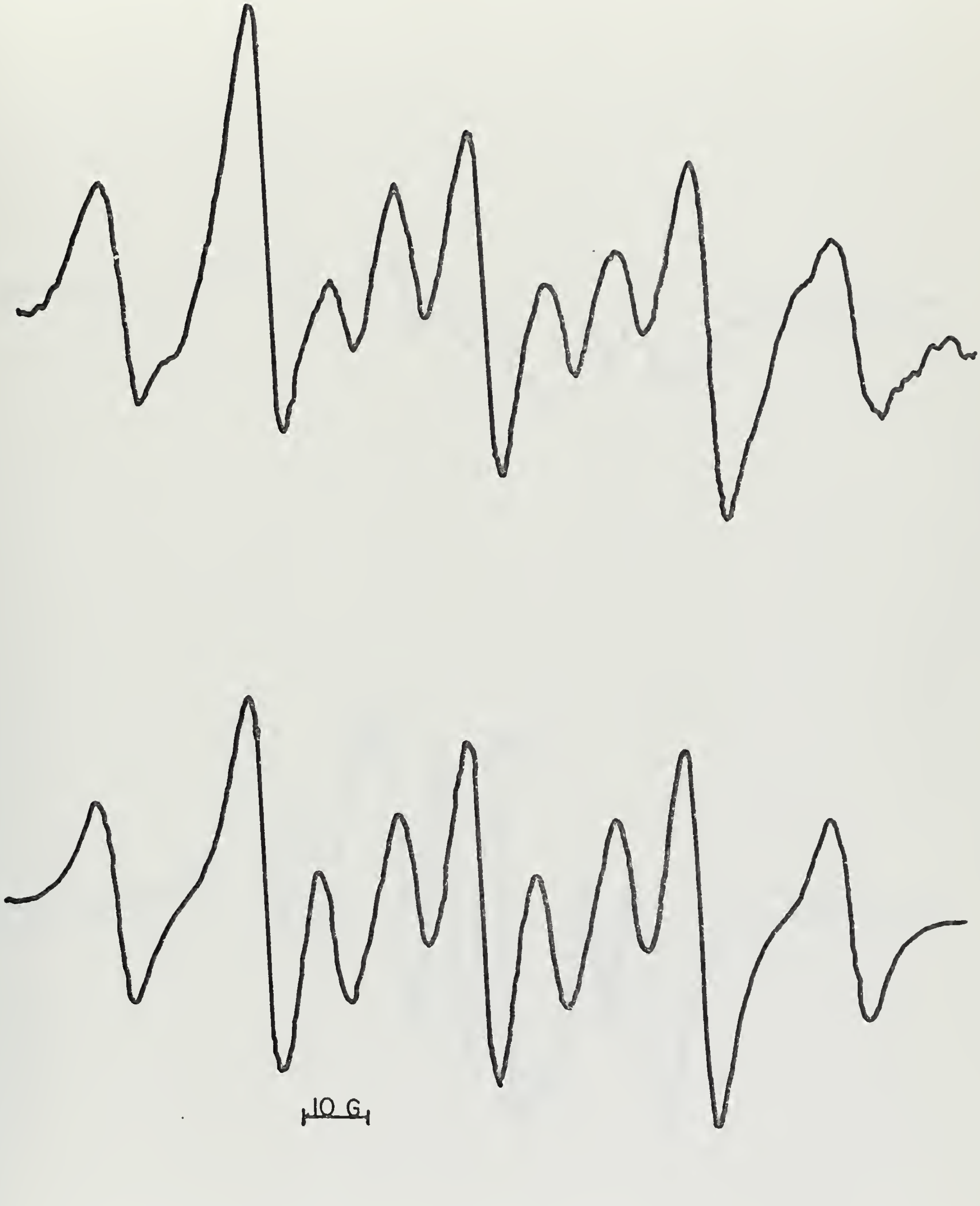

Figure 9. EPR Spectra - Applied Field Along the N^{14} Z Principal Axis. Top: Experimental Bottom: Simulated.

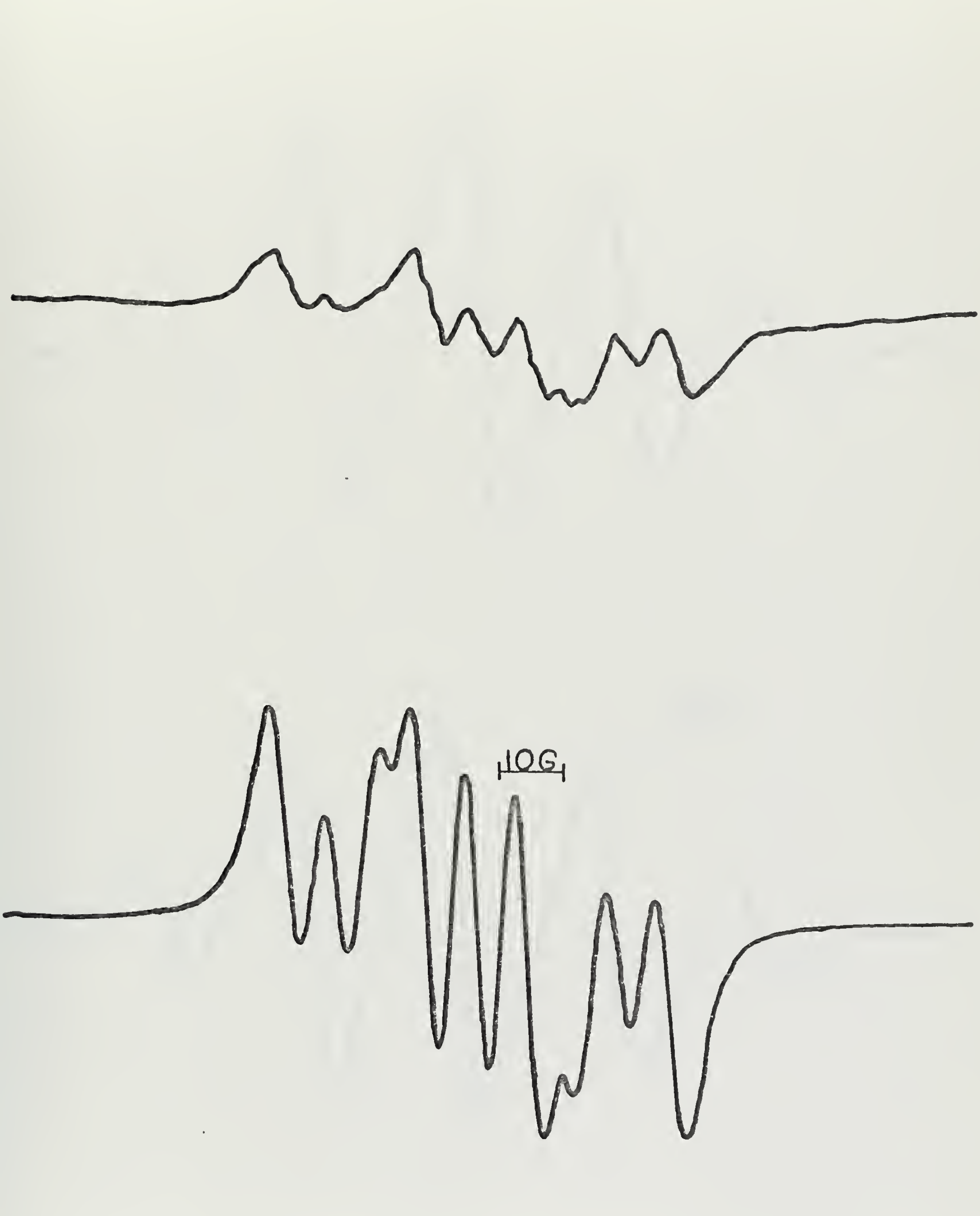

Figure 10. EPR Spectra - Applied Field Along the N^{14} Y Principal Axis. Top: Experimental Bottom: Simulated.

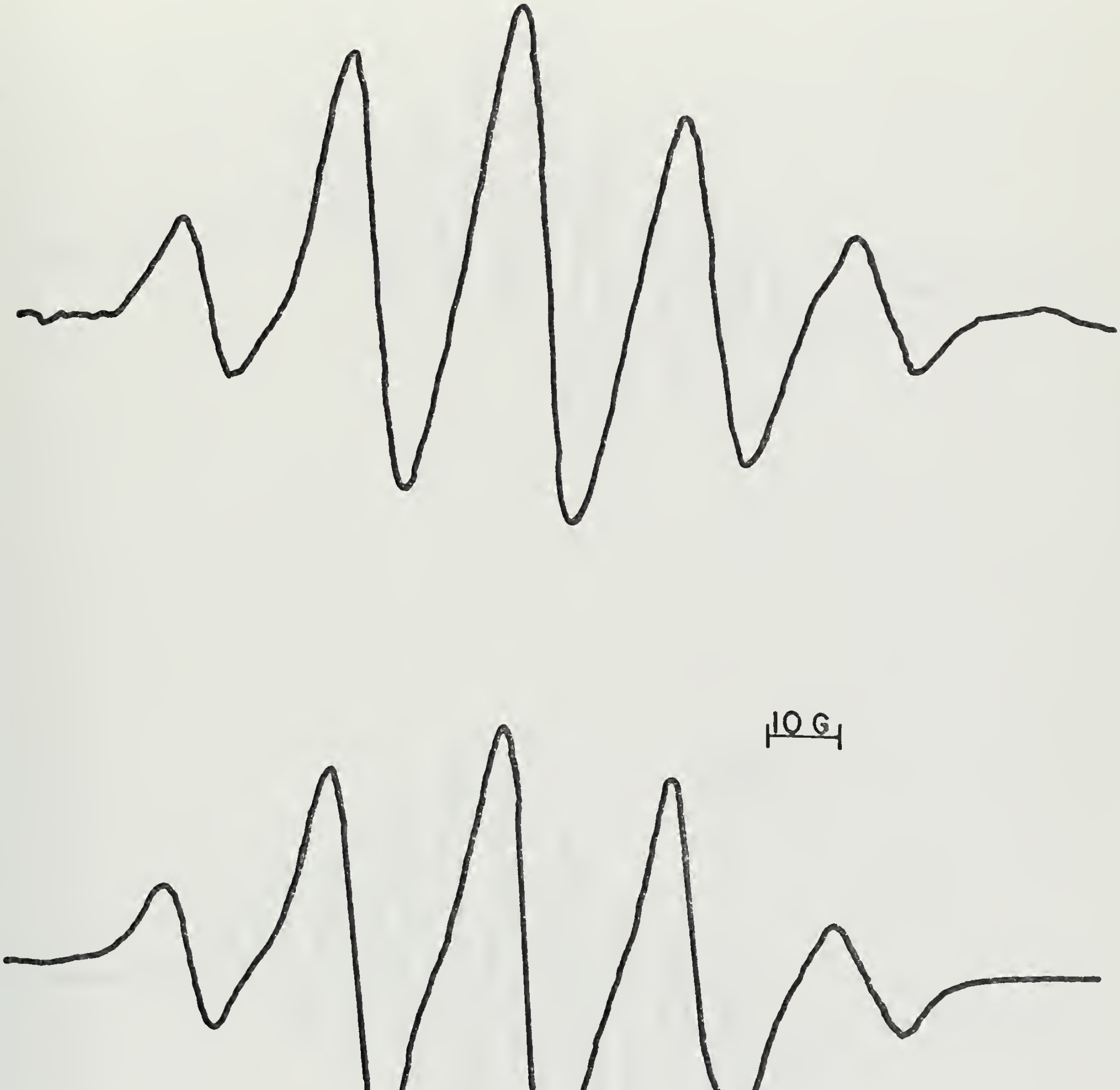

Figure 11. EPR Spectra - Applied Field Midway Between the N^{14} 2P Orbital and the N-O Bond in the YZ Principal Axis Plane. Top: Experimental Bottom: Simulated.

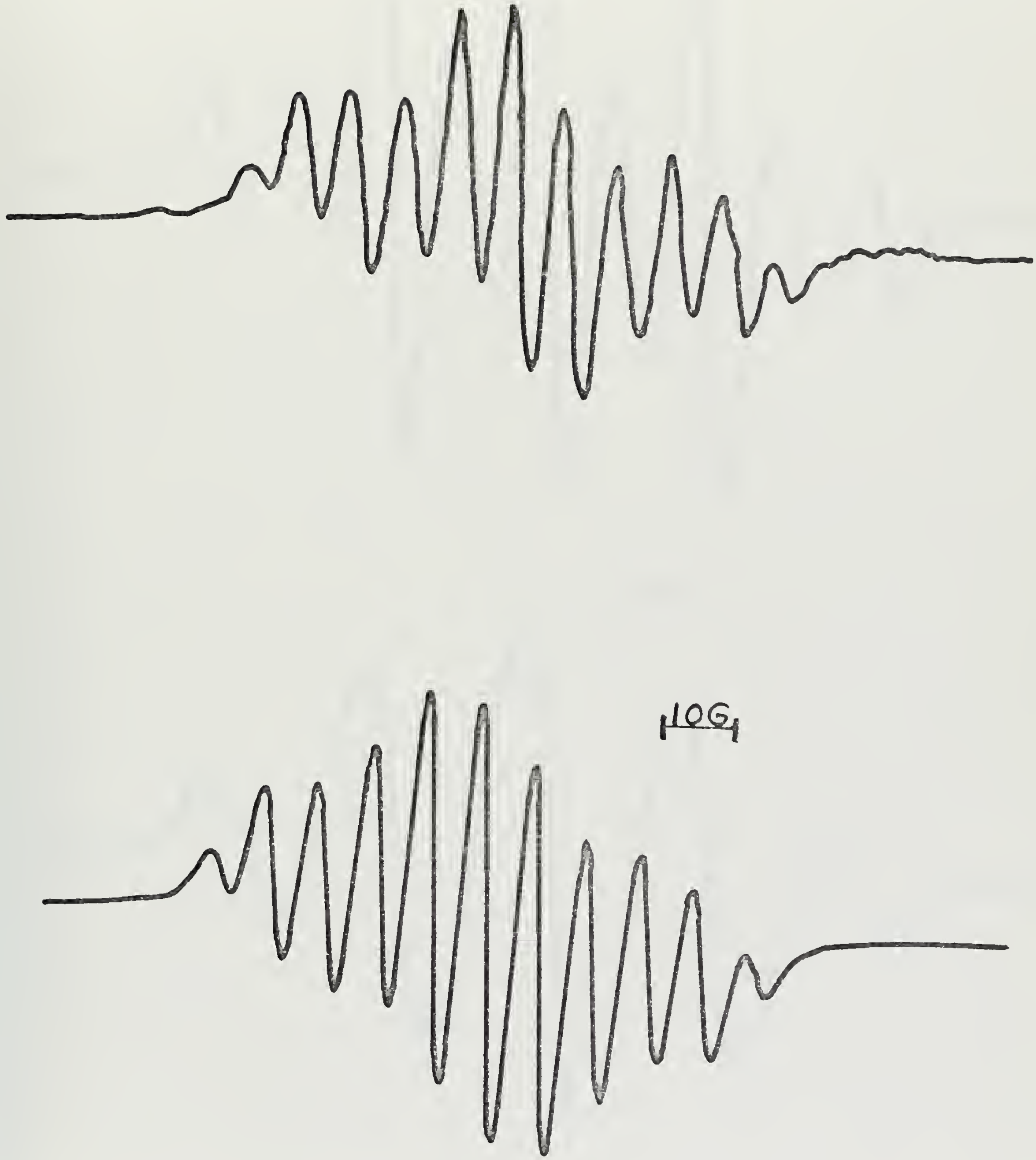

Figure 12. EPR Spectra - Applied Field Along the N^{14} X Principal Axis. Top: Experimental Bottom: Simulated.

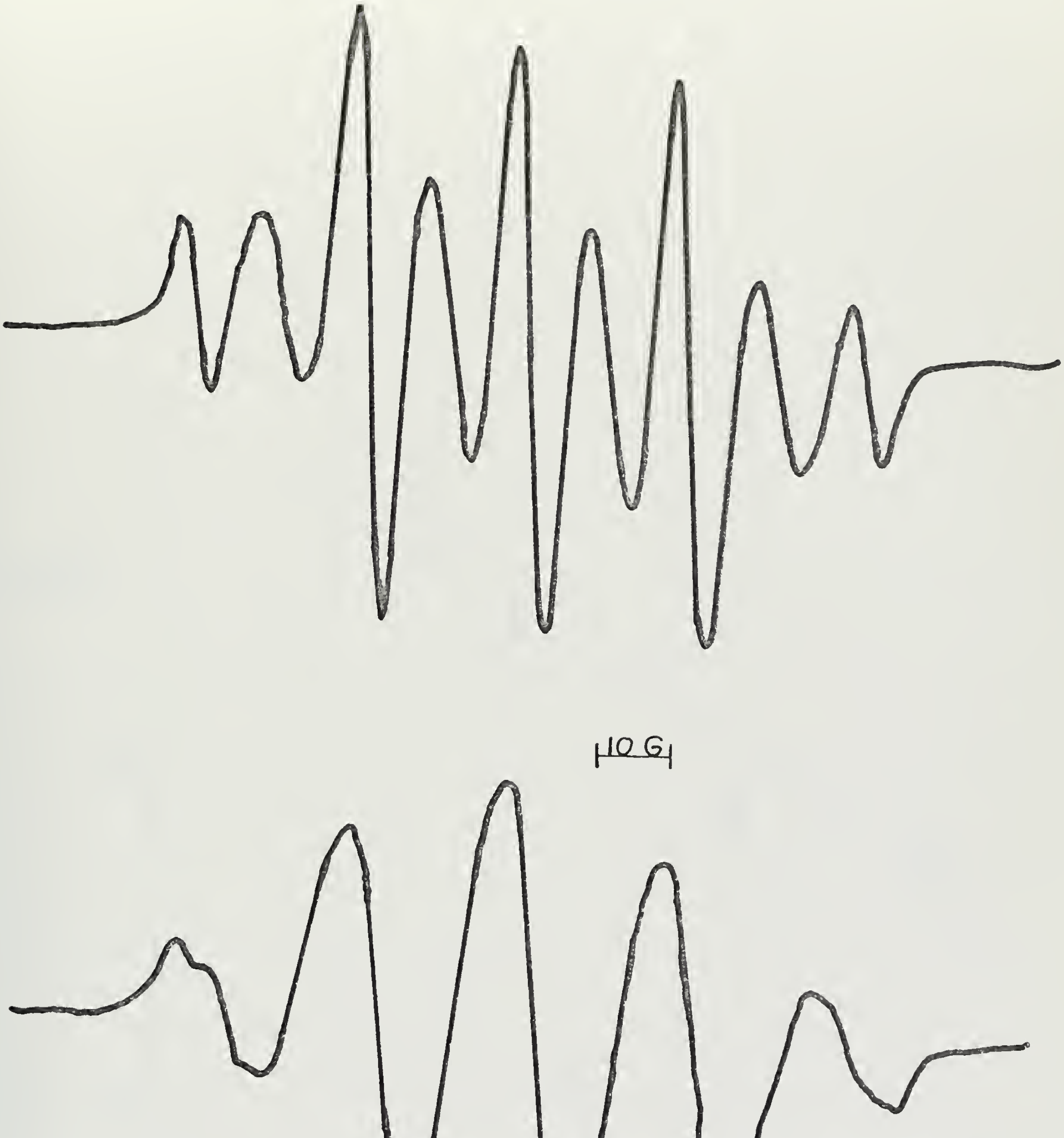

Figure 13. EPR Spectra - Applied Field Midway Between the X and the Z Principal Axes in the XZ Plane (Crystal Axis System Coordinates; $\theta=77.5$, $\phi=8.5$). Top: 29°C; Bottom: -15°C.

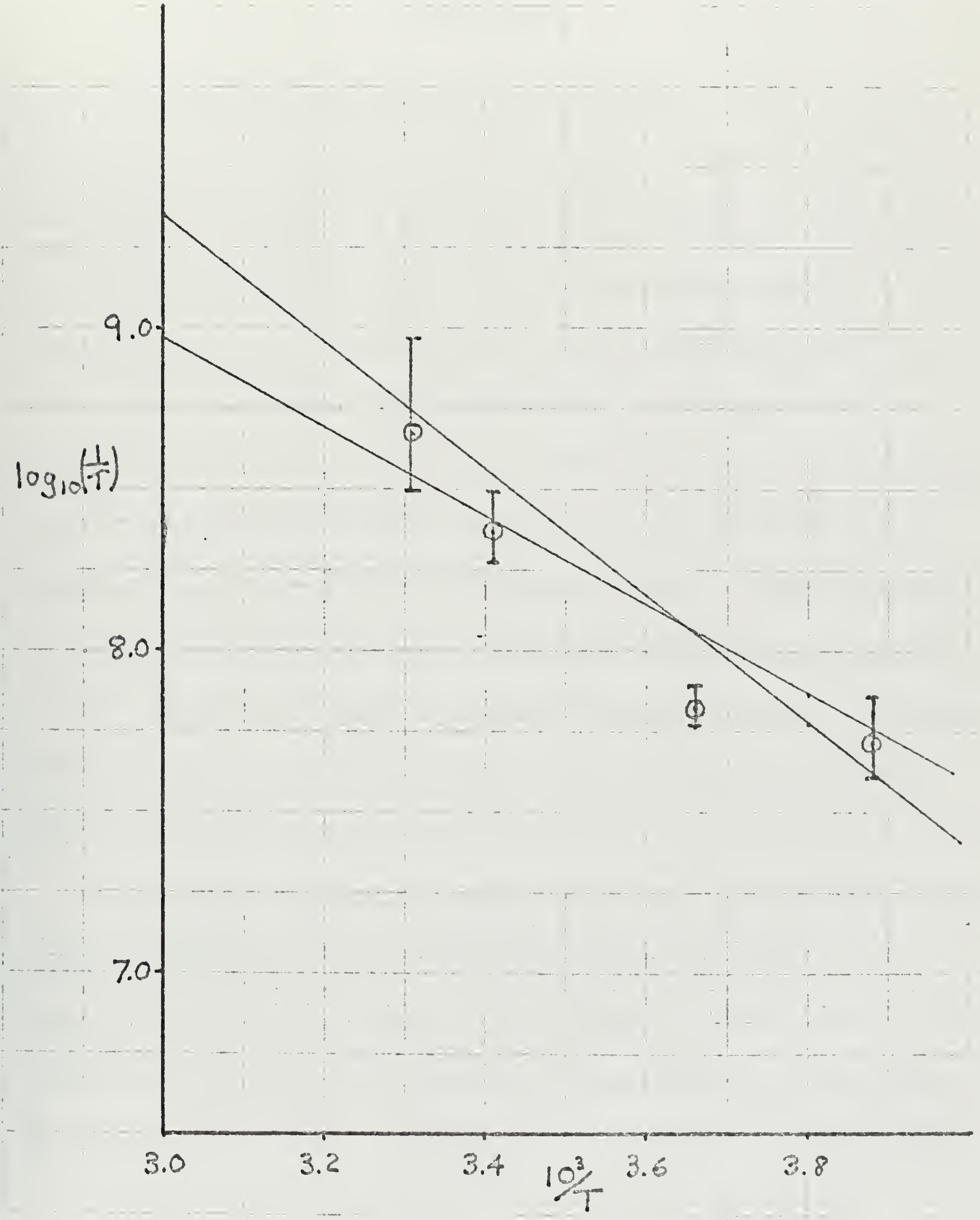

Figure 14. Arrhenius Rate Plot for Conformer Interconversion.

V. DISCUSSION

A. SUCCESS AND APPLICABILITY OF THE MODEL

Although the complex model used by program ESRPLT results in a very precise prediction of the individual line energies and intensities which compose an EPR spectrum, the more approximate approach of program NITROX gives plotted spectra which are indistinguishable from those produced by ESRPLT. This observation, combined with the fact that NITROX can be used to simulate a much wider variety of EPR spectra, makes NITROX the better choice as a tool for use in the study of paramagnetic system as typified by morpholine N-oxide. In fact, the extent to which the simulated spectra are reproductions of the experimentally observed spectra could only be enhanced by additional research directed toward the determination of separate direction cosine matrices for the axial and equatorial proton coupling tensors.

The possible applications of this experimental tool have been only partially explored during the research reported in this paper. It is adaptable to systems containing as many as two or as few as zero nitrogen nuclei, and it can include up to six equivalent or inequivalent protons in the treatment. It is particularly appropriate, in combination with program GEX, to the investigation of exchange phenomena.

It was observed that simulated spectra are very useful in the determination of coupling constants which are not otherwise measurable

because of poor resolution. A normal situation was that the N^{14} and axial proton coupling constants could be measured fairly accurately from experimental spectra, but the equatorial proton coupling constants usually had to be estimated. A few trials with program NITROX, using the measured and estimated coupling constants, usually resulted in the specification of a range of uncertainty for the estimated equatorial coupling constant of about one gauss.

B. REGARDING N^{14} HYPERFINE COUPLING

The observation that the average of the principal values of the N^{14} hyperfine coupling is the same at -150° C as at 20° C is very significant. It implies that the isotropic contribution (Fermi Contact) to the A-tensor does not change as the rate of exchange is decreased by a factor of at least ten (see section IV: E). In addition, the data show that the dipolar interaction increases along the Z principal axis and decreases along the X and Y principal axes as temperature is lowered.

C. SUGGESTIONS FOR FURTHER WORK

There is still much to be learned about the magnitudes and directions of the interactions which give rise to the observed EPR spectra of complex paramagnetic systems. The tools developed in this research can be used to extract much of this information. Some ideas for further research are:

1. Determine the direction cosines for the axial and equatorial proton coupling tensors at low temperatures (low rate of exchange). Use

these to determine the principal values of the axial and equatorial proton coupling tensors. It is expected that this information will be a very useful aid to the understanding of the Fermi Contact and dipolar interactions.

2. Combine programs NITROX and GEX so that, given the energies and intensities of the lines of the base spectrum for the case of no exchange, and given the predicted energies and intensities which simulate some experimentally observed spectrum, GEX computes the rate of exchange which must occur to cause the base spectrum to evolve into the observed one. This should result in an accurate prediction of the free energy, enthalpy, and entropy of activation for the process of conformer interconversion.

3. Progress to similar, complex paramagnetic systems.

D. SUMMARY AND CONCLUSIONS

1. A Useful Set of Tools

A set of research tools has been developed in the form of programs ESRPLT, NITROX and GEX, which should prove very useful in the exploration of complex paramagnetic systems. An especially useful feature of the spectra produced by NITROX and ESRPLT is that they are scaled so as to be superimposable on spectra recorded using the Varian spectrometer.

2. Comparison of Low and Room Temperature Hyperfine Coupling Constants

Table VII compares observed hyperfine coupling constants at room temperature with those observed at -150°C.

Table VII: Room Temperature versus -150°C
Hyperfine Coupling Constants for Morpholine N-oxide

Nucleus	Coupling Constant	Room Temp.	-150°C
N^{14}	A_{XX}	8.6 G	7.17 G
	A_{YY}	9.4 G	7.8 G
	A_{ZZ}	31.3 G	33.8 G
axial $H^{1,2}$	A_{XX}	13.6 G	23.0 G
	A_{YY}	11.3 G	21.8 G
	A_{ZZ}	11.4 G	23.3 G
equatorial $H^{1,2}$	A_{XX}	13.6 G	7.3 G
	A_{YY}	11.3 G	2.2 G
	A_{ZZ}	11.4 G	2.3 G

Notes:

(1) Hydrogen coupling constants at -150°C are those observed along the N^{14} principal axes. The near isotropy of the room temperature hydrogen coupling constants makes the comparison more significant than it might otherwise be.

(2) Exchange at room temperature results in the observation of an average value for the axial and equatorial hydrogen coupling constants.

3. Regarding Exchange

With the aid of program GEX, it was possible to simulate spectrum changes due to exchange phenomena, for spectra recorded in the temperature range from -150° to 29°C. The resulting data were used to compute the free energy of activation for the process of interconversion, and the data also led to reasonable estimates for the enthalpy and entropy of activation. The close agreement between the free energy value obtained in this research and the value obtained from EPR studies of morpholine N-oxide in methylene chloride leads to the conclusion that the mechanism for exchange is the same in solution as in the crystal matrix.

4. g-Tensor Anisotropy

It was possible, in this research, to observe the effects of g-tensor anisotropy in experimental spectra. An example of the disappearance of g-anisotropy with increasing rate of exchange is detectable in Figure 13. Note the slight asymmetry of the peaks at the opposite ends of the spectrum at -15°C. This asymmetry, which is attributable to g-anisotropy, had disappeared by the time the temperature had reached 29°C, as evidenced by the upper spectrum.

5. Alpha

The magnitude of the value determined for alpha means that the angular displacement of the N-0 bond is only five degrees above or below some mean plane described by the "average" direction of the N-0

bond and the two β carbon atoms. This would imply that only a small amount of motion occurs on the N-0 end of the molecule when conformation interconversion occurs.

APPENDIX A

MECHANICS OF ESRPLT

Most of the input parameters, and the mechanics of this program are covered by comments in the program itself. Several items, however, require additional clarification.

1. The Rotation Angles, Theta, Phi and Psi

The spatial relationship between crystal and principal axes may be expressed in a form other than the direction cosine matrix. The transformation of one axis system into another can be viewed as consecutive clockwise rotations about the X, Y, and Z axes of the reference system by the rotation angles theta, phi, and psi respectively, such that after the rotations have been accomplished, the two axis systems are superimposed. The rotations about the orthogonal axes of the reference system can be effected by a series of matrix operations. Once the proper rotation angles have been determined, the transformation matrices can be applied to vectors. Consider, for example, a unit vector expressed in terms of its components in the crystal axis system. If this unit vector is operated on by the proper transformation matrices, the resulting matrix will give the coordinates in the principal axis system, of each of the components of the vector. Shown below are the proper transformation matrices, operating on a vector with coordinates in the X, Y, Z system of 1_x, 1_y, 1_z.

$$\begin{bmatrix}\cos\psi & \sin\psi & 0\\ -\sin\psi & \cos\psi & 0\\ 0 & 0 & 1\end{bmatrix} \mathrm{X} \begin{bmatrix}\cos\phi & 0 & -\sin\phi\\ 0 & 1 & 0\\ \sin\phi & 0 & \cos\phi\end{bmatrix} \mathrm{X} \begin{bmatrix}1 & 0 & 0\\ \cos\theta & \sin\theta & 0\\ -\sin\theta & \cos\theta & 0\end{bmatrix}$$

rotation by ψ about Z axis

rotation by ϕ about Y axis

rotation by θ about X axis

$$\mathrm{X} \begin{bmatrix}1_X & 0 & 0\\ 0 & 1_y & 0\\ 0 & 0 & 1_z\end{bmatrix} = \begin{array}{ccc} \underline{1_x} & \underline{1_y} & \underline{1_z}\\ X'_x & X'_y & X'_z\\ Y'_x & Y'_y & Y'_z\\ Z'_x & Z'_y & Z'_z\end{array}$$

the vector in the X,Y,Z system

the vector in the X',Y',Z' system

That is, X'_x, Y'_x, Z'_x are the coordinates of 1_x in the prime system.

The three transformation matrices were combined into a single, total transformation matrix (TCOS). The rotation angles theta, phi, and psi which were used in both ESRPLT and NITROX were determined by setting each element of the total transformation matrix equal to the corresponding element of the appropriate direction cosine matrix. A computer program, LSTPP [9], was designed to calculate θ, ϕ, and ψ, using the method of least squares to give best fit values.

2. The Rotation Matrix RCOS

A matrix was developed which would simulate the effect of an angular displacement of the N-0 bond. This matrix, called RCOS, operated on the matrix TCOS. While TCOS was used to express the coordinates of a vector in the principal axis system, RCOS transformed

the coordinates so that they described the vector in a new principal axis system which has been displaced alpha degrees from the old one [10].

3. PTOP - Line Width

The peak-to-peak line width could be varied as necessary depending on the type of spectrum desired. It was found that PTOP = 0.015 gave good "stick" spectra, while PTOP = 0.25 seemed to work best for spectra simulation at -150°C. (Here PTOP is expressed in inches. The conversion factor to gauss is 0.06 inches/gauss.)

4. Scaling

The spectra which are plotted by this program are scaled at 15 inches/250 gauss, which is compatible with the spectrometer used in this research.

```
C                  PROGRAM ESRPLT
C  THIS PROGRAM COMPUTES AND PLOTS LOW TEMPERATURE ESR SPEC-
C  TRA IN THAT IT ASSUMES NO MOTIONAL EFFECTS.  THE PROGRAM
C  WAS DESIGNED TO SIMULATE ESR SPECTRA OF CYCLIC NITROXIDES
C  IT IS NOT LIMITED TO NITROXIDES, HOWEVER, AND IT CAN HAN-
C  DLE UP TO SIX NUCLEI WITH THEIR ASSOCIATED DIRECTION COS-
C  INES AND COUPLING CONSTANTS.  THE PROGRAM FORMULATES LINE
C  ENERGY AND INTENSITY MATRICES BY APPLYING THE HAMILTONIAN
C  H=G X BETA X HAPP DOT S + S DOT A DOT I - G(N) X BETA(N)
C  X HAPP DOT I TO SETS OF BASIS FUNCTIONS, THERE BEING ONE
C  SET OF BASIS FUNCTIONS FOR EACH ELECTRON-NUCLEUS PAIR.
C  THE RESULTING LINE ENERGY MATRICES ARE COMBINED, AS ARE
C  THE INTENSITY MATRICES, IN ORDER TO INTRODUCE HYPERFINE
C  COUPLING EFFECTS.  G-TENSOR ANISOTROPY IS INTRODUCED VIA
C  PRINCIPAL VALUES AND THE ROTATION ANGLES WHICH COME FROM
C  THE APPROPRIATE DIRECTION COSINE MATRIX.  THE ROTATION
C  ANGLES, THETA,PHI, AND PSI CORRESPOND TO CLOCKWISE ROTA-
C  TIONS ABOUT THE X,Y, AND Z AXES RESPECTIVELY (CRYSTAL
C  AXIS SYSTEM).
C  FORMAT OF INPUT DATA IS GIVEN AS FOLLOWS: CARD-LIST(FOR-
C  MAT)-DESCRIPTION
C  CARD 1 - NUMPTS,PTOP(I5,F5.2) - NUMPTS IS THE NO. OF
C         POINTS TO BE PLOTTED BY DRAW - PTOP IS THE SPEC-
C         TRUM LINE WIDTH
C  CARD 2 - PART2(6A8) - SECOND LINE OF THE PLOT TITLE
C  CARD 3 - ITIMES(I2) - THE NO. OF NUCLEI WHICH COUPLE WITH
C         THE UNPAIRED ELECTRON
C  CARD 4 - GX,GY,GZ(3F12.5) - PRINCIPAL VALUES OF THE
C         G-TENSOR
C  CARD 5 - SA(I,J),J=1,6 (6F12.5) - ROTATION ANGLES THETA,
C         PHI AND PSI FOLLOWED BY X,Y,Z PRINCIPAL VALUES OF
C         COUPLING CONSTANTS(IN THAT ORDER), FOR THE I-TH
C         NUCLEUS.  COUPLING CONSTANTS ARE ENTERED IN
C         INCHES(0.06INCHES/GAUSS)
C  CARD 6 - SXC(I),SSP(I),SAPH(I),SRTH(I),SRPH(I),SNT(I),
C         SIC(I) (5F12.5,2I5) - I IS THE ITH NUCLEUS.  SXC
C         IS THE MAGNITUDE OF THE APPLIED FIELD EXPRESSED
C         IN INCHES(250 GAUSS/15 INCHES =0.06 INCHES/GAUSS)
C         SSP IS THE NUCLEAR SPIN (EITHER 0.5 OR 1.0)
C         SAPH IS A DUMMY VARIABLE SET IT EQUAL TO 0.0
C         SRTH AND SRPH ARE THE THETA AND PHI POLAR CO-ORD
C         INATES(CRYSTAL AXIS SYSTEM) OF A VECTOR ABOUT
C         WHICH ROTATION BY THE ANGLE ALPHA OCCURS
C         SNT IS A COUNTER WHICH TELLS SUBROUTINE SYNTH HOW
C         LARGE THE TOTAL ENERGY AND INTENSITY MATRICES ARE
C         TO BE.  IT ALSO SERVES AS A DIRECTOR FOR INTRODUC
C         TION OF THE G-TENSOR.
C         SIC IS A DEBUGGING PARAMETER
C  CARD 7 - MODCUR,OFFSET,X,XB,ALPHA(I1,F4.1,3F10.1) -
C         MODCUR AND OFFSET ARE AS SPECIFIED BY SUBROUTINE
C         DRAW.
C         X=THETA FOR THE APPLIED FIELD(CRYSTAL AXIS SYS.)
C         XB=PHI FOR THE APPLIED FIELD(CRYSTAL AXIS SYS.)
C         ALPHA IS THE ANGLE BY WHICH THE DIRECTION COSINE
C         MATRIX IS ROTATED.
C
C
C  THE PROGRAM LOOPS BACK TO STATEMENT NO. 118 IN ORDER TO
C  ALLOW VARYING COMBINATIONS OF APPLIED FIELD ORIENTATION
C  AND ALPHA TO BE PLOTTED ON ONE GRAPH.  IF X(THETA)=0.0,
C  THE PROGRAM JUMPS TO STATEMENT NO. 1.  THIS ALLOWS A NEW
C  SET OF PARAMETERS TO BE READ IN FOR SOME DIFFERENT NUC-
C  LEUS, OR, MORE OFTEN, IT SETS THE PROGRAM UP FOR STARTING
C  A NEW SET OF PLOTS ON ANOTHER GRAPH.  IF NUMPTS=0, THE
C  PROGRAM TERMINATES
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 LABEL/8H        /
      INTEGER*4 SNT,SIC
      REAL*8 ITITLE(12),PART2(6),PART1(6)/'COMPUTER SIMULA-
     1TION OF EPR SPECTRUM WEERTS BOX W'/
      DIMENSION A(6),C(900),FEA(2304),FIA(2304),$D(900),
     1$C(900)
```

```
      DIMENSION SA(6,6),SXC(6),SSP(6),SAPH(6),SRTH(6),
     1SRPH(6),SNT(6),SIC(6)
      COMMON TDE(48,48),TINT(48,48),POSIT(1800),HITE(1800),
     1MDIM
      EQUIVALENCE (TDE(1,1),FEA(1)),(TINT(1,1),FIA(1))
      EQUIVALENCE (ITITLE(1),PART1(1)),(ITITLE(7),PART2(1))
    1 READ(5,112) NUMPTS,PTOP
  112 FORMAT (I5,F5.2)
      FLDMIN=-4.5
      FLDMAX=4.5
      $XSCAL=1.0
      $YSCAL=1.0
      IWIDE=9
      IHIGH=15
      IF(NUMPTS.EQ.0) STOP
      READ(5,111) PART2
  111 FORMAT (6A8)
      READ(5,113) ITIMES
  113 FORMAT (I2)
C  IF NITROGEN IS PRESENT IN THE MOLECULE, THE VALUES FOR N
C  MUST BE RUN THROUGH THE PROGRAM FIRST IN ORDER TO PROPER-
C  LY INTRODUCE THE EFFECT OF THE G TENSOR
C  IF THE VALUES FOR THE NITROGEN ARE TO BE READ IN FIRST,NT
C  MUST EQUAL, IN SUCCESSION, 1,3,6,12,24
C  READ IN THE PRINCIPAL VALUES OF THE G TENSOR
      READ(5,114) GX,GY,GZ
      WRITE(6,230) GX,GY,GZ
  114 FORMAT (3F12.5)
  230 FORMAT (' ',5X,'G-TENSOR PRINCIPAL VALUES'/
     1('',3(4X,F12,5)))
      DO 117 I=1,ITIMES
C THE COUPLING TENSORS AND THE ESR FREQUENCY(XC), ARE ENTER-
C  ED IN INCHES.  THE VALUES CORRESPONDING TO A(1-6) ARE,
C  RESPECTIVELY, THE ROTATION ANGLES THETA, PHI AND PSI,
C  AND THE X,Y,Z PRINCIPAL VALUES OF THE COUPLING TENSOR.
C  X(THETA) AND XB(PHI) SPECIFY THE DIRECTION OF THE MAG-
C  NETIC FIELC IN THE CRYSTAL AXIS SYSTEM.  FOR THE MEANING
C   OF NT, IC AND SP, SEE NPESR.  SIMILARLY FOR APH, RTH,
C  AND RPH, SEE ROTATE.   IF IT IS DESIRED TO SET THETA
C  (X)=0,PUT 0.0001 ON THE DATA CARD,NOT 0.0
      READ(5,115) (SA(I,J),J=1,6)
      READ(5,116) (SXC(I),SSP(I),SAPH(I),SRTH(I),SRPH(I),
     1SNT(1),SIC(1))
  115 FORMAT (6F12.5)
  116 FORMAT (5F12.5,2I5)
  117 CONTINUE
  118 READ(5,222) MODCUR,OFFSET,X,XB,ALPHA
  222 FORMAT(I1,F4.1,3F10.1)
      WRITE(6,223) MODCUR,OFFSET,X,XB,ALPHA
  223 FORMAT (' ','MODCUR,OFFSET,THETA,PHI,ALPHA'/
     1(' ',2X,I1,2X,4(F10.3)
      IF(X.EQ.0.0) GO TO 1
C  IF ALPHA IS GREATER THAN ZERO, WE RUN THRU ROTATE,NPESR
C  SNYTH, AND SHLSRT TWICE BEFORE GOING ON TO CURVE (ONCE
C  FOR +, AND ONCE FOR -, ALPHA).
      NX=2
      IF(ALPHA.EQ.0.0) NX=1
      DO 127 K=1,NX
      DO 219 I=1,ITIMES
      DO 213 J=1,6
  213 A(J)=SA(I,J)
      XC=SXC(I)
      SP=SSP(I)
      APH=ALPHA
      RTH=SRTH(I)
      RPH=SRPH(I)
      NT=SNT(I)
      IC=SIC(I)
  219 CALL ROTATE (A,X,XB,XC,SP,APH,RTH,RPH,NT,IC,GX,GY,GZ)
C IF IC=99, THE ENTIRE TDE AND TINT MATRICES WILL BE PRINT-
C  ED OUT.  SET IC=92 TO GET DATA PRINTED OUT.  SET IC=96 TO
C  GET DATA PLUS ALL  EXCEPT TDE AND TINT MATRICES
```

```
      IF(IC.GT.90) WRITE(6,139) (MODCUR,NUMPTS,PTOP,FLDMIN,
     1FLDMAX,$XSCAL,$YSCAL,IWIDE,IHIGH,ITIMES)
      IF(IC.NE.99) GO TO 125
C MDIM IS THE DIMENSION OF THE TRANSITION ENERGY AND TRANSI-
C  TION INTENSITY MATRICES WHICH RESULT WHEN ALL COUPLING
C  EFFECTS ARE TAKEN INTO ACCOUNT
  119 WRITE(6,122) ((I,J,TDE(I,J),J=1,MDIM),I=1,MDIM)
      DO 120 I=1,MDIM
  120 WRITE(6,123) (I,J,TINT(I,J),J=1,MDIM)
  122 FORMAT ('1',2X,'TDE'/(' ',6(I2,I2,2X,G13.6)))
  123 FORMAT (' ',2X,'TINT'/(' ',6(I2,I2,2X,G13.6)))
  125 N=MDIM*MDIM
      IT=0
      DO 126 I=1,MDIM
      DO 126 J=1,MDIM
      IT=IT+1
      FEA(IT)=TDE(J,I)
  126 FIA(IT)=TINT(J,I)
      CALL SHLSRT(N,IXHELD,ALPHA)
  127 ALPHA=-ALPHA
      WRITE(6,468) IXHELD
  468 FORMAT (' ','THE TOTAL NUMBER OF LINES IS'
     1/(' ',15))
      DO 128 I=1,1800
  128 C(I)=0.0
C  FIND THE INCREMENT BETWEEN POINTS ALONG THE Y AXIS
      DIFF=FLDMAX-FLDMIN
      FNUM1=NUMPTS-1
      FINCR=DIFF/FNUM1
      CALL CURVE(IXHELD,PTOP,FLDMIN,FLDMAX,FINCR,NUMPTS,C,
     1CMAX)
C  SCALE LINE INTENSITIES TO FIT ON PLOT
      DDCMX=2.0/CMAX
      DO 131 I=1,NUMPTS
      C(I)=C(I)*DDCMX
  131 C(I)=C(I)+OFFSET
C  SET THE POSITION FOR PLOTTING EACH VALUE OF C
      FLD=0.0
      DO 133 I=1,NUMPTS
      $D(I)=FLD
      $C(I)=C(I)
  133 FLD=FLD+FINCR
      CALL DRAW(NUMPTS,$D,$C,MODCUR,0,LABEL,ITITLE,$XSCAL,
     1$YSCAL,0,0,2,2,IWIDE,IHIGH,0,LAST)
      IF(LAST)134,135,134
  134 WRITE(6,137)
  135 GO TO 118
      STOP
  137 FORMAT (39H GRAPH NOT PLOTTED DUE TO ERROR IN DATA)
  139 FORMAT (' ',2I5,3F10.5,2F5.2,3I5)
      END


      SUBROUTINE ROTATE(A,X,XB,XC,SP,APH,RTH,RPH,NT,IC,GX,
     1GY,GZ)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(10),ECOS(3,3),AC(3),UH(3),R(4),TCOS(3,3),
     1RCOS(3,3),GCOS(3)
C  THIS PROGRAM ACCOMPLISHES THE FOLLOWING  IT FIRST
C  COMPUTES THE DIRECTION COSINE MATRIX,TCOS, FOR THE
C  COUPLING TENSOR IN THE CRYSTAL AXIS SYSTEM, USING THE
C  PRINCIPLL VALUES OF THE TENSOR AND THE ROTATION ANGLES
C  C  TH, PH, AND PS.  TCOS IS THEN OPERATED ON BY A
C  TRANSFORMATION MATRIX, RCOS, WHICH ACCOMPLISHES A ROTA-
C  TION BY AN ANGLE, ALPHA, ABOUT A VECTOR R.  R IS OF UNIT
C  LENGTH WITH ITS DIRECTION SPECIFIED IN THE CRYSTAL EXIS
C  SYSTEM BY RTH AND RPH.  THE RESULTANT DIRECTION COSINE
C  MATRIX, EXOS, IS USED TO COMPUTE DE AND FINT IN SUB-
C  ROUTINE NPESR.  TCOS,RCOS AND ECOS ARE ALL FORMED AS
C  MATRICES OF COMUMN VECTORS.
      CAR=3.1415926536/180.0
      FNMR=XC/658.2113
```

```
C   IF THE NUCLEUS IS NITROGEN, THE NMR FREQUENCY IS LESS
C   THAN FOR A PROTON
       IF(SP.EQ.1.0) FNMR=FNMR*3.076/42.576
       THETA=X*CAR
       PHI=XB*CAR
       TH=A(1)*CAR
       PH=A(2)*CAR
       PS=A(3)*CAR
       STHE=DSIN(THETA)
       SPHI=DSIN(PHI)
       CTHE=DCOS(THETA)
       CPHI=DCOS(PHI)
C   SPECIFY THE DIRECTION OF THE APPLIED FIELD IN THE CRYSTAL
C   AXIS SYSTEM
       UH(1)=STHE*CPHI
       UH(2)=STHE*SPHI
       UH(3)=CTHE
C   THE PRINCIPAL VALUES OF THE COUPLING TENSOR ARE
       AC(1)=A(4)
       AC(2)=A(5)
       AC(3)=A(6)
C   DO SOME GROUND WORK
       STH=DSIN(TH)
       SPH=DSIN(PH)
       SPS=DSIN(PS)
       CTH=DCOS(TH)
       CPH=DCOS(PH)
       CPS=DCOS(PS)
C   DEVELOP TCOS
       TCOS(1,1)=CPS*CPH
       TCOS(1,2)=SPS*CTH+CPS*STH*SPH
       TCOS(1,3)=SPS*STH-CPS*SPH*CTH
       TCOS(2,1)=-SPS*CPH
       TCOS(2,2)=CPS*CTH-SPS*SPH*STH
       TCOS(2,3)=CPS*STH+SPS*SPH*CTH
       TCOS(3,1)=SPH
       TCOS(3,2)=-CPH*STH
       TCOS(3,3)=CPH*CTH
       IF(IC.GT.95) WRITE(6,33) (((TCOS(I,J),J=1,3),I=1,3))
    33 FORMAT (' TCOS'/(' ',3G12.5))
C   SPECIFY A VECTOR PERPENDICULAR TO THE MAXIMUM EIGENVALUE
C   OF THE COUPLING TENSOR, OR IN ANY OTHER SUITABLE DIREC-
C   TION.
       RTH=RTH*CAR
       RPH=RPH*CAR
       R(1)=DSIN(RTH)*DCOS(RPH)
       R(2)=DSIN(RTH)*DSIN(RPH)
       R(3)=DCOS(RTH)
       DS=1.0-R(3)**2
       R(4)=DSQRT(DS)
C   ROTATE TCOS ABOUT R BY ANGLE ALPHA
       APH=APH*CAR
       APC=DCOS(APH)
       APS=DSIN(APH)
C   FORM THE RCOS MATRIX.  THIS MATRIX OPERATES ON TCOS AND
C   BASICALLY ACCOMPLISHES A ROTATION BY AN ANGLE ALPHA OF
C   ONE VECTOR ABOUT SOME OTHER ARBITRARY VECTOR.
       RCOS(1,1)=(APC*((R(1)*R(3))**2+R(2)**2))/DS+R(1)**2
       RCOS(1,2)=-R(1)*R(2)*APC+R(3)*APS+R(1)*R(2)
       RCOS(1,3)=-R(1)*R(3)*APC-R(2)*APS+R(1)*R(3)
       RCOS(2,1)=-R(1)*R(2)*APC-R(3)*APS+R(1)*R(2)
       RCOS(2,2)=(APC*(R(1)**2+(R(2)*R(3))**2))/DS+R(2)**2
       RCOS(2,3)=-R(2)*R(3)*APC+R(1)*APS+R(2)*R(3)
       RCOS(3,1)=-R(1)*R(3)*APC+R(2)*APS+R(1)*R(3)
       RCOS(3,2)=-R(2)*R(3)*APC-R(1)*APS+R(2)*R(3)
       RCOS(3,3)=DS*APC+R(3)**2
       IF(IC.GT.95) WRITE(6,34) (((RCOS(I,J),J=1,3),I=1,3))
    34 FORMAT (' RCOS'/(' ',3G12.5))
C   FORM ECOS MATRIX USING FORMAT REQUIRED BY NPESR
       DO 35 I=1,3
       DO 35 J=1,3
    35 ECOS(I,J)=RCOS(I,1)*TCOS(1,J)+RCOS(I,2)*TCOS(2,J)+
```

```
     1RCOS(I,3)*TCOS(3,J)
      HCORR=0.0
C  TRANSPOSE TO OBTAIN ROW VECTORS AS THAT IS WHAT NPESR
C  USES
   38 DO 39 I=1,3
      DO 39 J=I,3
      TEMP=ECOS(I,J)
      ECOS(I,J)=ECOS(J,I)
   39 ECOS(J,I)=TEMP
      IF(NT.GT.1) GO TO 41
      IF(SP.EQ.0.5) GO TO 41
C  GCOS IS THE DIRECTION COSINE MATRIX FOR THE G TENSOR
      DO 36 I=1,3
   36 GCOS(I)=UH(1)*ECOS(I,1)+UH(2)*ECOS(I,2)+UH(3)*
     1ECOS(1,3)
      GEFFS=(GX*GCOS(1))**2+(GY*GCOS(2))**2+(GZ*GCOS(3))**2
      GEFF=DSQRT(GEFFS)
      HCORR=HCORR+((2.002322-GEFF)/GEFF)*XC
   41 CALL NPESR (ECOS,AC,UH,FNMR,NT,IC,SP,HCORR)
      IF(IC.GT.90) WRITE(6,888) HCORR
  888 FORMAT ('   HCORR'/F12.8)
      RETURN
      END


      SUBROUTINE NPESR(ECOS,A,UH,H,NT,IC,SP,HCORR)
      IMPLICIT REAL*8(A-H,O-Z)
C  ECOS IS THE DIRECTION COSINE MATRIX.  ELEMENT J,K RELATES
C  THE COMPONENT OF THE J-TH PRINCIPAL AXIS ALONG THE K-TH
C  CRYSTAL AXIS.
C  A(J) IS THE J-TH PRINCIPAL VALUE.
C  UH(I) IS THE I-TH COMPONENT OF THE UNIT VECTOR POINTING
C  ALONG THE DIRECTION OF THE MAGNETIC FIELD
C  DE IS THE ARRAY OF TRANSITION FREQUENCIES CALCULATED
C  FINT IS THE CORRESPONDING ARRAY OF INTENSITIES
C  IC IS A DEBUGGING PARAMETER
C  SP IS THE NUCLEAR SPIN, EITHER 0.5 OR 1.0
      DIMENSION ECOS(3,3),A(3),UH(3),DE(3,3),FINT(3,3),
     1HV(3),HVP(2,3),HCOS(3),ABH(2),S(2),SS(3)
      IF(IC.LT.90) GO TO 5
      WRITE(6,101) (((ECOS(J,K),K=1,3),J=1,3))
      WRITE(6,102) (A(I),I=1,3)
      WRITE (6,103) (UH(I), I = 1,3)
  101 FORMAT (' ECOS'/(' ',3G12.5))
  102 FORMAT (' A',3G12.5)
  103 FORMAT (' UH',3G12.5)
    5 S(1) = 1.0
      S(2) = -1.0
      DO 10 J = 1,3
      HCOS(J)=0.0
      DO 10 K = 1,3
   10 HCOS(J)=HCOS(J)+UH(K)*ECOS(J,K)
      IF(IC.GT.95) WRITE (6,100) (HCOS(J),J=1,3)
      DO 15 J = 1,3
   15 HV(J)=0.0
      DO 20 J = 1,3
      CAS=HCOS(J)*A(J)
      DO 20 K = 1,3
   20 HV(K)=HV(K)+CAS*ECOS(J,K)
      IF(IC.GT.95) WRITE(6,100) (HV(J),J=1,3)
      DO 30 J = 1,2
      DO 30 K = 1,3
   30 HVP(J,K)=H*UH(K)-0.5*S(J)*HV(K)
      IF(IC.GT.95) WRITE(6,100) ((HVP(J,K),K=1,3),J=1,2)
      DO 40 J = 1,2
      ABH(J)=0.0
      DO 35 K = 1,3
   35 ABH(J)=ABH(J)+HVP(J,K)**2
   40 ABH(J)=DSQRT(ABH(J))
      IF(IC.GT.95) WRITE(6,100) (ABH(J),J=1,2)
      CE=0.0
      DO 45 J = 1,3
```

```
   45 CE=CE+HVP(1,J)*HVP(2,J)
   50 CE=CE/(ABH(1)*ABH(2))
      IF(IC.GT.95) WRITE(6,100) CE
      IF(SP.EQ.1.0) GO TO 58
      DO 54 J=1,2
      DO 54 K=1,2
      DE(J,K)=S(J)*ABH(1)-S(K)*ABH(2)
   54 DE(J,K)=0.5*DE(J,K)
      CT=(1.0+CE)/2.0
      ST=(1.0-CE)/2.0
      FINT(1,1)=1.0*CT
      FINT(1,2)=1.0*ST
      FINT(2,1)=FINT(1,2)
      FINT(2,2)=FINT(1,1)
      NS=2
      CALL SYNTH(DE,FINT,NT,NS,HCORR)
      IF(IC.GT.95) WRITE(6,105) ((I,J,DE(I,J),J=1,2),I=1,2)
      IF(IC.GT.95) WRITE(6,106) ((I,J,FINT(I,J),J=1,2),
     1I=1,2)
      GO TO 110
   58 SS(1)=1.0
      SS(2)=0.0
      SS(3)=-1.0
      SE=1.0-CE**2
      DO 59 J=1,3
      DO 59 K=1,3
   59 DE(J,K)=SS(J)*ABH(1)-SS(K)*ABH(2)
      CX=CE
      SX=SE/2.0
      CX1=((1.0+CX)/2.0)**2
      CX2=((1.0-CX)/2.0)**2
      CX3=CX**2
      FINT(1,1)=1.0*CX1
      FINT(1,2)=1.0*SX
      FINT(1,3)=1.0*CX2
      FINT(2,1)=FINT(1,2)
      FINT(2,2)=1.0*CX3
      FINT(2,3)=FINT(1,2)
      FINT(3,1)=FINT(1,3)
      FINT(3,2)=FINT(1,2)
      FINT(3,3)=FINT(1,1)
      NS=3
      CALL SYNTH(DE,FINT,NT,NS,HCORR)
      IF(IC.GT.95) WRITE(6,107) ((I,J,DE(I,J),J=1,3),I=1,3)
      IF(IC.GT.95) WRITE(6,108)  ((I,J,FINT(I,J),J=1,3),
     1I=1,3)
  100 FORMAT(1H,10F11.5)
  105 FORMAT (' ',13X,'DE'/(' ',2(I2,I2,2X,G12.5)))
  106 FORMAT (' ',12X,'FINT'/(' ',2(I2,I2,2X,G12.5)))
  107 FORMAT (' ',15X,'DE'/(' ',3(I2,I2,2X,G12.5)))
  108 FORMAT (' ',15X,'FINT'/(' ',3(I2,I2,2X,G12.5)))
  110 RETURN
      END


      SUBROUTINE SYNTH(DE,FINT,NT,NS,HCORR)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DE(3,3),FINT(3,3)
      COMMON TDE(48,48),TINT(48,48),POSIT(1800),HITE(1800),
     1MDIM
C TDE IS THE RESULTANT TRANSITION ENERGY MATRIX
C TINT IS THE RESULTANT TRANSITION INTENSITY MATRIX
C NT IS THE PRESENT DIMENSION OF TDE AND TINT
C NS IS THE DIMENSION OF THE INCOMING DE AND FINT MATRICES
C NT*NS IS THE NEW DIMENSION FOR TDE AND TINT
C  SET THE INITIAL VALUES FOR TDE AND TINT
      IF(NT-1)85,85,88
   85 DO 86 I=1,48
      DO 86 J=1,48
      TDE(I,J)=HCORR
   86 TINT(I,J)=1.0
      DO 87 I=1,NS
```

```
      DO 87 J=1,NS
      TDE(I,J)=HCORR+DE(I,J)
   87 TINT(I,J)=FINT(I,J)
      GO TO 92
C  READY
   88 M=NT*NS
      NT1=NT+1
      NS1=NS+1
      N=NT*NS
      DO 91 I=1,NT
      NR=NT1-I
      DO 91 J=1,NT
      NC=NT1-J
      BENG=TDE(NR,NC)
      BLIN=TINT(NR,NC)
      DO 90 K=1,NS
      KR=NS1-K
      DO 90 L=1,NS
      LC=NS1-L
      TDE(M,N)=BENG+DE(KR,LC)
      TINT(M,N)=BLIN*FINT(KR,LC)
      N=N-1
      IF(N-1)89,90,90
   89 M=M-1
      N=NT*NS
   90 CONTINUE
   91 CONTINUE
   92 MDIM=NT*NS
      RETURN
      END


      SUBROUTINE SHLSRT(N,IXHELD,ALPHA)
      REAL*8 SPEC/0.001/,TEMP,RTEMP,FEA(2304),FIA(2304),
     1POSIT(1800),HITE(1800)
      COMMON FEA,FIA,POSIT,HITE,MDIM
C    N IS EQUAL TO MDIM SQUARED
C  THIS SUBROUTINE FIRST ELIMINATES ALL LINES WITH INTENSITY
C  LESS THAN SPEC FOR BOTH + AND - ALPHA.  THEN IT ARRANGES
C  THE LINES IN ORDER OF INCREASING ENERGY IN THE ARRAY
C  POSIT
C  FIRST ELIMINATE ALL LINES WITH INTENSITY LESS THAN SPEC
      J=1
      DO 450 I=1,N
      IF(FIA(I)-SPEC) 450,445,445
  445 FIA(J)=FIA(I)
      FEA(J)=FEA(I)
      IX=J
      J=J+1
  450 CONTINUE
      WRITE(6,189) IX
C  IF ALPHA IS GT.OR EQ. 0.0, STORE THE ELEMENTS OF FEA AND
C  FIA IN THE FIRST IX SPACES OF POSIT AND HITE
      IF(ALPHA.LT.0.0) GO TO 444
      IXHOLD=1
  444 IXHELD=IXHOLD+IX-1
      J=0
      DO 448 I=IXHOLD,IXHELD
      J=J+1
      POSIT(I)=FEA(J)
  448 HITE(I)=FIA(J)
      IXHOLD=IXHELD+1
C  IF ALPHA IS GREATER THAN ZERO AT THIS POINT, WE NEED TO
C  GO BACK AND GET THE LINES CORRESP TO NEG ALPHA BEFORE
C  ARRANGING LINES IN ORDER OF INCREASING ENERGY.
      IF(ALPHA.GT.0.0) GO TO 186
      M1=1
  145 M1=M1*2
      IF(M1-IXHELD) 145,145,150
  150 M1=M1/2-1
      MM=M1
  152 MM=MM/2
```

```
      IF(MM) 187,186,154
  154 K=IXHELD-MM
      IF(K) 187,187,156
  156 DO 170 J=1,K
      II=J
  158 IM=II+MM
      IF(POSIT(IM)-POSIT(II)) 160,170,170
  160 TEMP=POSIT(II)
      RTEMP=HITE(II)
      POSIT(II)=POSIT(IM)
      HITE(II)=HITE(IM)
      POSIT(IM)=TEMP
      HITE(IM)=RTEMP
      II=II-MM
      IF(II) 170,170,158
  170 CONTINUE
      GO TO 152
  186 RETURN
  187 WRITE(6,190) MM,K,II,J
  189 FORMAT(' ','THE NUMBER OF LINES WITH INTENSITY GT.
     10.001 IS',I5)
  190 FORMAT(' ',20H PROGRAM ERROR      ,4I10)
      STOP 1
      END


      SUBROUTINE CURVE(IXHELD,PTOP,FLDMIN,FLDMAX,FINCR,
     1NUMPTS,C,CMAX)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON FEA(2304),FIA(2304),POSIT(1800),HITE(1800),MDIM
      DIMENSION C(1800)
C  THIS SUBROUTINE FORMS THE FIRST DERIVATIVE LORENTZIAN
C  LINE SHAPE , USING THOSE LINES WHICH FALL WITHIN THE
C  FIELD WIDTH SPECIFIED.
      W=PTOP*0.8660254
      WS=W*W
      FLD=FLDMIN-FINCR
      CMAX=0.0
      PTOPM=8.0*PTOP
      IMIN=1
      IMAX=1
      DO 220 I=1,NUMPTS
      FLD=FLD+FINCR
      FMIN=FLD-PTOPM
      FMAX=FLD+PTOPM
  195 IF(POSIT(IMIN)-FMIN) 196,200,200
  196 IF(IMIN-IXHELD) 197,200,200
  197 IMIN=IMIN+1
      GO TO 195
  200 IF(POSIT(IMAX)-FMAX) 201,205,205
  201 IF(IMAX-IXHELD) 202,205,205
  202 IMAX=IMAX+1
      GO TO 200
  205 DO 210 J=IMIN,IMAX
      AJ=POSIT(J)-FLD
      DENOM=WS+AJ*AJ
  210 C(I)=C(I)+(HITE(J)*WS*AJ)/(DENOM*DENOM)
      IF(DABS(C(I))-CMAX) 220,220,215
  215 CMAX=DABS(C(I))
  220 CONTINUE
      RETURN
      END
```

APPENDIX B

MECHANICS OF NITROX

The input parameters to program NITROX are nearly identical to those of ESRPLT. The most significant difference is in the meaning of the parameter SIC (or IC). In this program it gives the case number for the i-th nucleus. The case number specifies the nuclear spin of the i-th nucleus, and it also designates the number of equivalent nuclei of the i-th kind.

RCOS, TCOS, PTOP, and scaling are as in ESRPLT. The comments at the beginning and throughout the program give an adequate description of what the program does.

```
C                     PROGRAM NITROX
C  THIS PROGRAM COMPUTES COUPLING CONSTANTS FOR A NITROXIDE
C  AS A FUNCTION OF THE DIRECTION OF THE APPLIED FIELD.  THE
C  COUPLING CONSTANTS ARE FORMULATED USING PRINCIPAL VALUES
C  OF THE COUPLING CONSTANTS, THE DIRECTION OF THE APPLIED
C  FIELD, AND THE DIRECTION COSINE MATRIX WHICH REPRESENTS
C  THE DIRECTIONS OF THE PRINCIPAL AXES IN THE CRYSTAL AXIS
C  SYSTEM FOR THE PARTICULAR NUCLEUS OF INTEREST.  NITROX
C  ALSO PREDICTS AND PLOTS FIRST ORDER ESR SPECTRA USING THE
C  HIGH FIELD APPROXIMATION.  THE ESR SPECTRUM IS CONSTRUCT-
C  ED BY COMBINING THE COMPUTED COUPLING CONSTANTS, USING
C  APPROPRIATE LEVELS OF PASCALS'TRIANGLE TO SPECIFY SPLIT-
C  TINGS AND INTENSITIES FOR THE PROTONS, SUPERIMPOSING
C  THESE SPLITTINGS ON THE 1:1:1 SPLITTING DUE TO THE NITRO-
C  GEN NUCLEUS.
C  IN ADDITION TO THE PLOTTED OUTPUT, NITROX ALSO PUNCHES
C  CARDS WHICH CONTAIN THE SPECTRUM LINE ENERGIES AND INTEN-
C  SITIES.  THE FORMAT OF THESE CARDS IS SET SO THAT THEY
C  CAN BE USED AS INPUT DATA FOR PROGRAM GEX.
C  NITROX WAS DESIGNED PRIMARILY TO SIMULATE ESR SPECTRA OF
C  CYCLIC NITROXIDES, BUT IT IS ADAPTABLE FOR RADICALS WITH
C  UP TO SIX EQUIVALENT (OR INEQUIVALENT) PROTONS WITHOUT
C  MODIFICATION.  IT CAN ALSO DEAL WITH THE CASE OF TWO
C  EQUIVALENT NITROGEN NUCLEI WITHOUT MODIFICATION.
C  G-TENSOR ANISOTROPY IS INTRODUCED VIA PRINCIPAL VALUES
C  AND THE ROTATION ANGLES WHICH COME FROM THE DIRECTION
C  COSINE MATRIX WHICH REPRESENTS THE PRINCIPAL AXES OF THE
C  G-TENSOR IN THE CRYSTAL AXIS SYSTEM.  THE ROTATION ANGLES
C  THETA, PHI AND PSI CORRESPOND TO CLOCKWISE ROTATIONS
C  ABOUT THE X,Y AND Z AXES RESPECTIVELY (CRYSTAL AXIS SYS)
C  DATA CARDS ARE DESCRIBED AS FOLLOWS: CARD NO. - NAME LIST
C  (FORMAT) - DESCRIPTION
C  CARD 1 - ITIMES,NOSETS,NUMPTS,PTOP(3I5,F10.5) - ITIMES IS
C         THE NO. OF NUCLEI WHICH COUPLE WITH THE FREE ELEC-
C         TRON. NOSETS IS THE NUMBER OF SETS OF INEQUIVALENT
C         NUCLEI IN THE MOLECULE.  NUMPTS IS THE NO. OF
C         POINTS TO BE PLOTTED BY DRAW. PTOP IS THE SPECTRUM
C         LINE WIDTH.
C  CARD 2 - PART2 (6A8) - SECOND LINE OF THE PLOT TITLE
C  CARD 3 - GX,GY,GZ (3F12.5) - PRINCIPAL VALUES OF THE
C         G-TENSOR.
C  CARD 4 - SA(I,J),J=1,6 (6F12.5) - ROTATION ANGLES THETA,
C         PHI AND PSI FOLLOWED BY X,Y,Z PRINCIPAL VALUES OF
C         COUPLING CONSTANTS(IN THAT ORDER), FOR THE I-TH
C         NUCLEUS.
C  CARD 5 - SXC(I),SAPH(I),SRTH(I),SRPH(I),SIC(I)(4F12.5,I5)
C         I IS THE I-TH NUCLEUS. SXC IS THE MAGNITUDE OF THE
C         APPLIED FIELD.
C  ALL COUPLING CONSTANTS AND THE APPLIED FIELD ARE ENTERED
C  IN INCHES(250 GAUSS/15 INCHES=0.06 INCHES/GAUSS.)
C         SAPH IS A CARRY-OVER ENTER 0.0  SRTH AND SRPH ARE
C         THE POLAR CO-ORDINATES OF A UNIT VECTOR ABOUT
C         WHICH ROTATION BY THE ANGLE ALPHA OCCURS.  SIC IS
C         THE NUCLEUS CASE NUMBER.
C  THERE WILL BE I SETS OF CARDS 4 AND 5 BEFORE CARD(S) 6
C  CARD 6 - MODCUR,OFFSET,X,XB,ALPHA(I1,F4.1,3F10.1) - MOD-
C         CUR AND OFFSET ARE AS SPECIFIED BY SUBROUTINE DRAW
C         X(THETA) AND XB (PHI) SPECIFY THE DIRECTION OF THE
C         APPLIED FIELD IN THE CRYSTAL AXIS SYSTEM.  ALPHA
C         IS THE ANGLE BY WHICH THE DIRECTION COSINE MATRIX
C         IS ROTATED
C
C
C  THE PROGRAM LOOPS BACK TO STATEMENT NO. 118 IN ORDER TO
C  ALLOW VARYING COMBINATIONS OF APPLIED FIELD ORIENTATION
C  AND ALPHA TO BE PLOTTED ON ONE GRAPH.  IF X(THETA)=0.0,
C  THE PROGRAM JUMPS TO STATEMENT NO. 1. THIS ALLOWS A NEW
C  SET OF PARAMETERS TO BE READ IN FOR SOME DIFFERENT NUC-
C  LEUS, OR, MORE OFTEN, IT SETS THE PROGRAM UP FOR STARTING
C  A NEW SET OF PLOTS ON ANOTHER GRAPH.  IF ITIMES=0, THE
C  PROGRAM TERMINATES.
      IMPLICIT REAL*8 (A-H,O-Z)
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      REAL*8 ITITLE(12),PART2(6),PART1(6)/'EPR SPECTRUM
     1PRINCIPAL LINES ONLY'/
      REAL*8 LABEL/8H        /
      INTEGER*4 SIC
      DIMENSION SA(6,6),SXC(6),SAPH(6),SRTH(6),SRPH(6),
     1SIC(6),CA(6),A(100),FIA(100),C(900),$C(900),$D(900)
      COMMON SPLT(12),A,FIA,ICASE(12)
      EQUIVALENCE (ITITLE(1),PART1(1)),(ITITLE(7),PART2(1))
    1 READ(5,113) ITIMES,NOSETS,NUMPTS,PTOP
      IF(ITIMES.EQ.0) STOP
  113 FORMAT (3I5,F10.5)
      FLDMIN=-4.5
      FLDMAX=4.5
      $XSCAL=1.0
      $YSCAL=1.0
      IWIDE=9
      IHIGH=15
C PART2 IS THE 2ND LINE OF THE PLOT TITLE
      READ(5,111) PART2
  111 FORMAT (6A8)
C  IF NITROGEN IS PRESENT IN THE MOLECULE, THE VALUES FOR N
C  MUST BE RUN THRU THE PROGRAM FIRST IN ORDER TO PROPERLY
C  INTRODUCE THE EFFECT OF THE G-TENSOR
C  THIS PROGRAM PREDICTS THE COUPLING CONSTANTS FOR A NIT-
C  ROXIDE AS A FUNCTION OF THE DIRECTION OF THE APPLIED
C  FIELD.  IT ALSO COMPUTES THE POSITIONS AND INTENSITIES OF
C  THE LINES OF THE FIRST-ORDER SPECTRUM.
C  IC SERVES AS A NUCLEUS CASE NUMBER INDICATOR.
C  IC=1 FOR 1 H, 2 FOR 2 EQUIV H'S, ETC THRU 6, IC=7 FOR 1
C  NITROGEN AND 8 FOR 2 EQUIV NITROGENS.  NUCNUM IS A NUC-
C  LEUS COUNTER.
C  READ IN THE PRINCIPAL VALUES OF THE G TENSOR
      READ(5,114) GX,GY,GZ
      WRITE(6,230) GX,GY,GZ
  114 FORMAT (3F12.5)
  230 FORMAT (' ',5X,'G-TENSOR PRINCIPAL VALUES'/
     1(' ',3(4X,F12.5)))
      DO 117 I=1,ITIMES
C THE COUPLING TENSORS AND THE ESR FREQUENCY(XC), ARE EN-
C  TERED IN INCHES.  THE VALUES CORRESP TO CA(1-6) ARE, RES-
C  PECTIVELY, THE ROTATION ANGLES THETA,PHI AND PSI, AND THE
C  X,Y,Z PRINCIPAL VALUES OF THE COUPLING TENSOR.  X(THETA)
C  AND XB(PHI) SPECIFY THE DIRECTION OF THE MAGNETIC FIELD
C  IN THE CRYSTAL AXIS SYSTEM.
C  IF IT IS DESIRED TO SET THETA(X)=0, PUT 0.0001 ON THE
C  DATA CARD, NOT 0.0
      READ(5,115) (SA(I,J),J=1,6)
      READ(5,116) (SXC(I),SAPH(I),SRTH(I),SRPH(I),SIC(I))
  115 FORMAT (6F12.5)
  116 FORMAT (4F12.5,I5)
  117 CONTINUE
  118 READ(5,222) MODCUR,OFFSET,X,XB,ALPHA
  222 FORMAT(I1,F4.1,3F10.1)
      WRITE(6,223) MODCUR,OFFSET,X,XB,ALPHA
  223 FORMAT (' ','MODCUR,OFFSET,THETA,PHI,ALPHA'/
     1(' ',2X,I1,2X,4(F10.3)))
      IF(X.EQ.0.0) GO TO 1
      NX=2
      IF(ALPHA.EQ.0.0) NX=1
      NZ=0
      DO 127 K=1,NX
      DO 219 I=1,ITIMES
      DO 213 J=1,6
  213 CA(J)=SA(I,J)
      XC=SXC(I)
      APH=ALPHA
      RTH=SRTH(I)
      RPH=SRPH(I)
      IC=SIC(I)
      NUCNUM=I
  219 CALL ROTATE (CA,X,XB,XC,APH,RTH,RPH,IC,GX,GY,GZ,
     1NUCNUM,NOSETS)
```

```
      CALL CALCSP(NOSETS,NO)
      WRITE(6,232) (A(I),FIA(I),I=1,NO)
      NZ=NZ+NO
      IF(ALPHA.LE.0.0) GO TO 127
      J=28
      DO 126 I=1,NZ
      A(J)=A(I)
      FIA(J)=FIA(I)
  126 J=J+1
  127 ALPHA=-ALPHA
      WRITE(7,700) X,XB,ALPHA
  700 FORMAT (3F10.2)
      WRITE(7,701) (A(I),I=1,NZ)
      WRITE(7,701) (FIA(I),I=1,NZ)
  701 FORMAT (16F5.2)
      CALL SHLSRT(NZ)
C   FIND THE INCREMENT BETWEEN POINTS ALONG THE Y AXIS
      DIFF=FLDMAX-FLDMIN
      FNUM1=NUMPTS-1
      FINCR=DIFF/FNUM1
      DO 129 I=1,1800
  129 C(I)=0.0
      CALL CURVE(NZ,PTOP,FLDMIN,FLDMAX,FINCR,NUMPTS,C,CMAX)
      WRITE(6,233) (A(I),FIA(I),I=1,NZ)
      WRITE(6,234) NZ
C   SCALE LINE INTENSITIES TO FIT ON PLOT
      DDCMX=2.0/CMAX
      DO 131 I=1,NUMPTS
      C(I)=C(I)*DDCMX
  131 C(I)=C(I)+OFFSET
      FLD=0.0
      DO 133 I=1,NUMPTS
      $D(I)=FLD
      $C(I)=C(I)
  133 FLD=FLD+FINCR
      CALL DRAW(NUMPTS,$D,$C,MODCUR,0,LABEL,ITITLE,$XSCAL,
     1$YSCAL,0,0,2,2,IWIDE,IHIGH,0,LAST)
      IF(LAST)134,135,134
  134 WRITE(6,137)
  135 GO TO 118
  137 FORMAT('    ERROR IN DATA')
  232 FORMAT (' ','ENERGY-INTENSITY'/(' ',8F12.5))
  233 FORMAT (' ','COMBINED ENERGY-INTENSITY'/(' ',8F12.5))
  234 FORMAT (' ','TOTAL NO. OF LINES IS'/(' ',I5))
      STOP
      END


      SUBROUTINE ROTATE(CA,X,XB,XC,APH,RTH,RPH,IC,GX,GY,GZ,
     1NUCNUM,NOSETS)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION CA(10),ECOS(3,3),AC(3),UH(3),R(4),TCOS(3,3),
     1RCOS(3,3),GCOS(3)
      COMMON SPLT(12),A(100),FIA(100),ICASE(12)
C   THIS PROGRAM ACCOMPLISHES THE FOLLOWING  IT FIRST COM-
C   PUTES THE DIRECTION COSINE MATRIX, TCOS, FOR THE COUPLING
C   TENSOR IN THE CRYSTAL AXIS SYSTEM, USING THE PRINCIPAL
C   VALUES OF THE TENSOR AND THE ROTATION ANGLES, TH, PH AND
C   PS.  TCOS IS THEN OPERATED ON BY A TRANSFORMATION MATRIX,
C   RCOS, WHICH ACCOMPLISHES A ROTATION BY AN ANGLE ALPHA
C   ABOUT A VECTOR R.  R IS OF UNIT LENGTH WITH ITS DIRECTION
C   SPECIFIED IN THE CRYSTAL AXIS SYSTEM BY RTH AND RPH.
C   THE RESULTING DIRECTION COSINE MATRIX, ECOS, IS TRANS-
C   POSED SO THAT IT BECOMES A MATRIX OF ROW VECTORS.  COUP-
C   LING CONSTANTS ARE THEN CALCULATED.
      CAR=3.1415926536/180.0
      FNMR=XC/658.2113
      THETA=X*CAR
      PHI=XB*CAR
      TH=CA(1)*CAR
      PH=CA(2)*CAR
      PS=CA(3)*CAR
```

```
      STHE=DSIN(THETA)
      SPHI=DSIN(PHI)
      CTHE=DCOS(THETA)
      CPHI=DCOS(PHI)
C  SPECIFY THE DIRECTION OF THE APPLIED FIELD IN THE CRYSTAL
C  AXIS SYSTEM.
      UH(1)=STHE*CPHI
      UH(2)=STHE*SPHI
      UH(3)=CTHE
C  THE PRINCIPAL VALUES OF THE COUPLING TENSOR ARE
      AC(1)=CA(4)
      AC(2)=CA(5)
      AC(3)=CA(6)
C  DO SOME GROUND WORK
      STH=DSIN(TH)
      SPH=DSIN(PH)
      SPS=DSIN(PS)
      CTH=DCOS(TH)
      CPH=DCOS(PH)
      CPS=DCOS(PS)
C  DEVELOP TCOS
      TCOS(1,1)=CPS*CPH
      TCOS(1,2)=SPS*CTH+CPS*STH*SPH
      TCOS(1,3)=SPS*STH-CPS*SPH*CTH
      TCOS(2,1)=-SPS*CPH
      TCOS(2,2)=CPS*CTH-SPS*SPH*STH
      TCOS(2,3)=CPS*STH+SPS*SPH*CTH
      TCOS(3,1)=SPH
      TCOS(3,2)=-CPH*STH
      TCOS(3,3)=CPH*CTH
      WRITE(6,33) (((TCOS(I,J),J=1,3),I=1,3))
   33 FORMAT (' TCOS'/(' ',3G12.5))
C  SPECIFY A VECTOR ABOUT WHICH THE ROTATION IS TO OCCUR.
      RTH=RTH*CAR
      RPH=RPH*CAR
      R(1)=DSIN(RTH)*DCOS(RPH)
      R(2)=DSIN(RTH)*DSIN(RPH)
      R(3)=DCOS(RTH)
      DS=1.0-R(3)**2
      R(4)=DSQRT(DS)
C  ROTATE TCOS ABOUT R BY ANGLE ALPHA
      APH=APH*CAR
      APC=DCOS(APH)
      APS=DSIN(APH)
C  FORM THE RCOS MATRIX
      RCOS(1,1)=(APC*((R(1)*R(3))**2+R(2)**2))/DS+R(1)**2
      RCOS(1,2)=-R(1)*R(2)*APC+R(3)*APS+R(1)*R(2)
      RCOS(1,3)=-R(1)*R(3)*APC-R(2)*APS+R(1)*R(3)
      RCOS(2,1)=-R(1)*R(2)*APC-R(3)*APS+R(1)*R(2)
      RCOS(2,2)=(APC*(R(1)**2+(R(2)*R(3))**2))/DS+R(2)**2
      RCOS(2,3)=-R(2)*R(3)*APC+R(1)*APS+R(2)*R(3)
      RCOS(3,1)=-R(1)*R(3)*APC+R(2)*APS+R(1)*R(3)
      RCOS(3,2)=-R(2)*R(3)*APC-R(1)*APS+R(2)*R(3)
      RCOS(3,3)=DS*APC+R(3)**2
      WRITE(6,34) (((RCOS(I,J),J=1,3),I=1,3))
   34 FORMAT (' RCOS'/(' ',3G12.5))
C  FORM ECOS MATRIX USING FORMAT REQUIRED BY NPESR
      DO 35 I=1,3
      DO 35 J=1,3
   35 ECOS(I,J)=RCOS(I,1)*TCOS(1,J)+RCOS(I,2)*TCOS(2,J)+
     1RCOS(I,3)*TCOS(3,J)
      HCORR=0.0
C  TRANSPOSE TO OBTAIN ROW VECTORS AS THAT IS WHAT NPESR
C  USES.
   38 DO 39 I=1,3
      DO 39 J=I,3
      TEMP=ECOS(I,J)
      ECOS(I,J)=ECOS(J,I)
   39 ECOS(J,I)=TEMP
C  GCOS IS ESSENTIALLY THE DIRECTION COSINE OF THE MAGNETIC
C  FIELD IN THE PRINCIPAL AXIS SYSTEM.
      DO 36 I=1,3
```

```
   36 GCOS(I)=UH(1)*ECOS(I,1)+UH(2)*ECOS(I,2)+UH(3)*
     1ECOS(I,3)
      IF(NUCNUM.GT.1) GO TO 41
      GEFFS=(GX*GCOS(1))**2+(GY*GCOS(2))**2+(GZ*GCOS(3))**2
      GEFF=DSQRT(GEFFS)
      HCORR=HCORR+((2.002322-GEFF)/GEFF)*XC
      WRITE(6,888) HCORR
      DO 510 I=1,27
  510 A(I)=HCORR
   41 AEFFS=(AC(1)*GCOS(1))**2+(AC(2)*GCOS(2))**2+
     1(AC(3)*GCOS(3))**2
      SPLT(NUCNUM)=DSQRT(AEFFS)
      ICASE(NUCNUM)=IC
      WRITE(6,890) NUCNUM,SPLT(NUCNUM),ICASE(NUCNUM)
  888 FORMAT ('     HCORR'/F12.8)
  890 FORMAT (' ','NUCLEUS COUPLING CONSTANT  CASE NO.'/
     1(' ',2X,I2,4X,F10.3,4X,I2))
      RETURN
      END


      SUBROUTINE CALCSP(NOSETS,NO)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION IN(8,8),SP(8,8)
      COMMON SPLT(12),A(100),FIA(100),ICASE(12)
      DATA IN/3,4,5,6,7,8,4,6,9*1,2,3,4,5,6,1,2,0,1,3,6,10,
     115,1,3,0,0,1,4,10,20,0,2,3*0,1,5,15,0,1,4*0,1,6,7*0,1,
     22*0/,SP/8*0.,-.5,-1.,-1.5,-2.,-2.5,-3.,-1.,-2.,.5,0.,
     3-.5,-1.,-1.5,-2.,0.,-1.,0.,1.,.5,0.,-0.5,-1.,1.,3*0.,
     41.5,1.,0.5,2*0.,1.,3*0.,2.,1.5,1.,0.,2.,4*0.,2.5,2.,
     57*0.,3.,2*0./
      FIA(1) = 1.0
      NO=1
      NOJ=1
      NOK = 2
      DO 50 I=1,NOSETS
      IC = ICASE(I)
      IQ = IN(IC,1)
      IQ2=IQ+2
      NO = NO*(IQ-1)
      NOI=NO+1
      DO 30 J = 1,NOJ
      NOK = NOK-1
      DO 20 K = 2,IQ
      NOI = NOI-1
      IQ2K = IQ2-K
      A(NOI) = A(NOK)+SP(IC,IQ2K)*SPLT(I)
   20 FIA(NOI) = FIA(NOK)*IN(IC,IQ2K)
   30 CONTINUE
      NOK = NO+1
      NOJ = NO
   50 CONTINUE
      FMAX = 0.0
      DO 60 I = 1,NO
      IF(FIA(I).LE.FMAX) GO TO 60
      FMAX = FIA(I)
   60 CONTINUE
      DO 65 I = 1,NO
   65 FIA(I) = FIA(I)/FMAX
      RETURN
      END


      SUBROUTINE SHLSRT (N)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON SPLT(12),A(100),FIA(100),ICASE(12)
      M1 = 1
    6 M1 = M1*2
      IF(M1-N) 6,6,8
    8 M1 = M1/2-1
      MM=M1
   20 MM= MM/2
```

```
      IF(MM) 99,100,21
   21 K = N-MM
      IF(K ) 99,99,22
   22 DO 1 J=1,K
      II=J
   11 IM=II+MM
      IF(A(IM)-A(II)) 30,1,1
   30 TEMP = A(II)
      RTEMP= FIA(II)
      A(II)=A(IM)
      FIA(II)= FIA(IM)
      A(IM)= TEMP
      FIA(IM)= RTEMP
      II = II-MM
      IF(II) 1,1,11
    1 CONTINUE
      GO TO 20
  100 RETURN
   99 WRITE(6,999) MM,K,II,J
  999 FORMAT(   20H PROGRAM ERROR        4I10 )
      END


      SUBROUTINE CURVE (IX,PTOP,FLDMIN,FLDMAX,FINCR,NUMPTS,
     1C,CMAX)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON SPLT(12),A(100),FIA(100),ICASE(12)
      DIMENSION C(1800)
C  THIS SUBROUTINE FORMS THE FIRST DERIVATIVE LORENTZIAN
C  LINE SHAPE , USING THOSE LINES WHICH FALL WITHIN THE
C  FIELD WIDTH SPECIFIED.
      W=PTOP*0.8660254
      WS=W*W
      FLD=FLDMIN-FINCR
      CMAX=0.0
      PTOPM=8.0*PTOP
      IMIN=1
      IMAX=1
      DO 220 I=1,NUMPTS
      FLD=FLD+FINCR
      FMIN=FLD-PTOPM
      FMAX=FLD+PTOPM
  195 IF(A(IMIN)-FMIN) 196,200,200
  196 IF(IMIN-IX) 197,200,200
  197 IMIN=IMIN+1
      GO TO 195
  200 IF(A(IMAX)-FMAX) 201,205,205
  201 IF(IMAX-IX) 202,205,205
  202 IMAX=IMAX+1
      GO TO 200
  205 DO 210 J=IMIN,IMAX
      AJ=A(J)-FLD
      DENOM=WS+AJ*AJ
  210 C(I)=C(I)+(FIA(J)*WS*AJ)/(DENOM*DENOM)
      IF(DABS(C(I))-CMAX) 220,220,215
  215 CMAX=DABS(C(I))
  220 CONTINUE
      RETURN
      END
```

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13. ABSTRACT

Low temperature (-150°C) EPR spectra of the nitroxide generated photolytically in a single crystal of N-nitromorpholine are complicated by the presence of two magnetically distinct orientations of the N-0 bond within the crystal. As the temperature is raised, the spectra are further complicated by motional effects. Since at -150° the molecule is essentially frozen in the crystal lattice with respect to the time of the EPR interaction, and since the nitrogen coupling tensor is markedly anisotropic, the observed EPR spectrum varies widely as the orientation of the applied field changes. The anisotropy of the nitrogen coupling tensor made it possible to unequivocally determine the orientation of the crystal with respect to the applied magnetic field. A series of experimental spectra was then obtained for several combinations of crystal orientation and temperature. In addition, computer programs were developed which simulate low, intermediate, and high temperature EPR spectra. By using a combination of experimental spectra and these programs, it was possible to determine the angle between the two orientations of the N-0 bond in the crystal and also to determine the energy barrier to exchange.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nitroxide of N-nitromorpholine						
Electron Paramagnetic Resonance						
Electron Spin Resonance						
Morpholine N-oxide						

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